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(54) Title: POLYMERIZABLE COMPOSITIONS CONTAINING ALKOXYAMINE COMPOUNDS DERIVED FROM NITROSO- OR NITRONE COMPOUNDS			
<div style="text-align: center;"> </div> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> (1) </div> <div style="text-align: center;"> (a) </div> <div style="text-align: center;"> (b) </div> </div>			
(57) Abstract A polymerizable composition, comprising a) at least one ethylenically unsaturated monomer or oligomer, and b) an initiator compound of formula (I) wherein n is 0 or 1. The compounds of formula (I) are prepared from a free radical (a) and a compound of formula R10NO or (b). Further aspects of the present invention are a process for polymerizing ethylenically unsaturated monomers, novel initiator compounds and their use for polymerization, intermediate compounds and also the polymer or copolymer produced by this process.			

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Polymerizable Compositions Containing Alkoxyamine Compounds Derived From Nitroso- Or Nitrone Compounds

The present invention relates to a polymerizable composition comprising a) at least one ethylenically unsaturated monomer and b) a nitroxide initiator compound. Further aspects of the present invention are a process for polymerizing ethylenically unsaturated monomers, novel initiator compounds and their use for polymerization, and also the polymer or copolymer produced by this process.

More specifically, in one of its aspects the present invention relates to polymerizable compositions and polymerization processes which provide polymeric resin products having low polydispersity, which polymerization processes proceed with enhanced monomer to polymer conversion efficiencies. In particular, this invention relates to stable free radical-mediated polymerization processes which provide homopolymers, random copolymers, block copolymers, multiblock copolymers, graft copolymers and the like, at enhanced rates of polymerization and enhanced monomer to polymer conversions.

Polymers or copolymers prepared by free radical polymerization processes inherently have broad molecular weight distributions or polydispersities which are generally higher than about four. One reason for this is that most of the free radical initiators have half lives that are relatively long, ranging from several minutes to many hours, and thus the polymeric chains are not all initiated at the same time and the initiators provide growing chains of various lengths at any time during the polymerization process. Another reason is that the propagating chains in a free radical process can react with each other in processes known as combination and disproportionation, both of which are irreversibly chain-terminating reaction processes. In doing so, chains of varying lengths are terminated at different times during the reaction process, resulting in resins consisting of polymeric chains which vary widely in length from very small to very large and which thus have broad polydispersities. If a free radical polymerization process is to be used for producing narrow molecular weight distributions, then all polymer chains must be initiated at about the same time and termination of the growing polymer-chains by combination or disproportionation processes must be avoided.

Conventional radical polymerization reaction processes pose various significant problems, such as difficulties in predicting or controlling the molecular weight, the polydispersity and

the modality of the polymers produced. These prior art polymerization processes produce polymers having broad polydispersities and in some instances, low polymerization rates. Furthermore, free radical polymerization processes in bulk of the prior art are difficult to control because the polymerization reaction is strongly exothermic and an efficient heat removal in the highly viscous polymer is mostly impossible. The exothermic nature of the prior art free radical polymerization processes often severely restricts the concentration of reactants or the reactor size upon scale-up.

Due to the above mentioned uncontrollable polymerization reactions, gel formation in conventional free radical polymerization processes are also possible and cause broad molecular weight distributions and/or difficulties during filtering, drying and manipulating the product resin.

US-A-4 581 429 to Solomon et al., issued April 8, 1986, discloses a free radical polymerization process which controls the growth of polymer chains to produce short chain or oligomeric homopolymers and copolymers, including block and graft copolymers. The process employs an initiator having the formula (in part) $R'R''N-O-X$, where X is a free radical species capable of polymerizing unsaturated monomers. The reactions typically have low conversion rates. Specifically mentioned radical $R'R''N-O\cdot$ groups are derived from 1,1,3,3 tetraethylisoindoline, 1,1,3,3 tetrapropylisoindoline, 2,2,6,6 tetramethylpiperidine, 2,2,5,5 tetramethylpyrrolidine or di-t-butylamine.

EP-A-735 052 discloses a method of preparing thermoplastic polymers of narrow polydispersities by free radical-initiated polymerization, which comprises adding a free radical initiator and a stable free radical agent to the monomer compound.

This method has the disadvantage that uncontrollable recombinations of initiator radicals occur immediately after their formation, thus producing variable ratios between initiator radicals and stable free radicals. Consequently there is not enough control about the polymerization process.

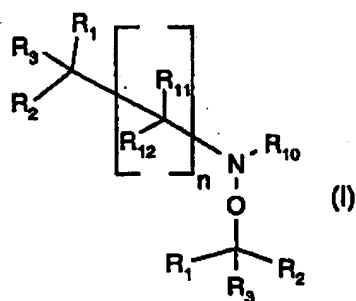
There is therefore still a need for polymerization processes for the preparation of narrow polydispersity polymeric resins with defined molecular weights using the economical free radical polymerization techniques. These polymerization processes will also control the physical properties of the polymers such as viscosity, hardness, gel content, processability, clarity, high gloss, durability, and the like.

The polymerization processes and resin products of the present invention are useful in many applications, including a variety of specialty applications, such as for the preparation of block copolymers which are useful as compatibilizing agents for polymer blends, or dispersing agents for coating systems or for the preparation of narrow molecular weight resins or oligomers for use in coating technologies and thermoplastic films or as toner resins and liquid immersion development ink resins or ink additives used for electrophotographic imaging processes.

Surprisingly, it has now been found that it is possible to overcome the afore mentioned shortcomings of the prior art by providing a polymerizable composition containing specific initiator compounds. The majority of these compounds are novel and they are also an object of the present invention. Polymerization of the composition results in a polymer or copolymer of narrow polydispersity and a high monomer to polymer conversion even at relatively low temperatures and at short reaction times, making the polymerization process particularly suitable for industrial applications. The resulting copolymers are of high purity and in many cases colourless, therefore not requiring any further purification.

One object of the present invention is to provide a polymerizable composition, comprising

- a) at least one ethylenically unsaturated monomer or oligomer, and
- b) an initiator compound of formula (I)



wherein n is 0 or 1

R₁, R₂, R₃ are each independently of one another hydrogen, halogen, NO₂, cyano, -CONR₅R₆, -(R₉)COOR₄, -C(O)-R₇, -OR₈, -SR₈, -NHR₈, -N(R₈)₂, carbamoyl, di(C₁-C₁₈alkyl)carbamoyl, -C(=NR₅)(NHR₆);

unsubstituted C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or R₂ and R₃, together with the linking carbon atom, form a C₃-C₁₂cycloalkyl radical, a (C₄-C₁₂cycloalkanon)-yl radical or a C₃-C₁₂cycloalkyl radical containing at least one O atom and/or a NR₈ group; or if n is 1



R₄ is hydrogen, C₁-C₁₈alkyl, phenyl, an alkali metal cation or a tetraalkylammonium cation; R₅ and R₆ are hydrogen, C₁-C₁₈alkyl, C₂-C₁₈alkyl which is substituted by at least one hydroxy group or, taken together, form a C₂-C₁₂alkylene bridge or a C₂-C₁₂alkylene bridge interrupted by at least one O or/and NR₈ atom;

R₇ is hydrogen, C₁-C₁₈alkyl or phenyl;

R₈ is hydrogen, C₁-C₁₈alkyl or C₂-C₁₈alkyl which is substituted by at least one hydroxy group;

R₉ is C₁-C₁₂alkylene or a direct bond;

R₁₀ is C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, C₉-C₁₁phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, C₉-C₁₁phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;

if n is 1

R₁₁ is C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R₁₀ and R₁₁ together form a C₂-C₁₂alkylene bridge, a C₃-C₁₂alkylen-on bridge or a C₂-C₁₂alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C₁-C₁₈alkyl, hydroxy(C₁-C₄)alkyl, phenyl, C₇-C₉phenylalkyl, NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino,

R₁₂ is hydrogen, -(R₈)COOR₄, cyano, -OR₈, -SR₈, -NHR₈, -N(R₈)₂, -NH-C(O)-R₈, unsubstituted C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino; or

R₁₁ and R₁₂ together with the linking carbon atom form a C₃-C₁₂cycloalkyl radical; with the proviso that bis-(2-cyano-2-propyl)-N-phenylhydroxylamine is excluded and if n = 0 R₁₀ is different from the group -CR₁R₂R₃.

The initiator compound of formula (I) is preferably present in an amount of 0.01 mol-% to 30 mol-%, more preferably in an amount of 0.1 mol-% to 10 mol-% and most preferably in an amount of 0.1 to 5 mol-%, based on the monomer, oligomer or monomer/oligomer mixture used.

Preferably compounds of formula (I) do not contain the structural element 2,2,6,6 tetra(C₁-C₄alkyl)piperidine, 2,2,5,5 tetra(C₁-C₄alkyl)pyrrolidin or 1,1,3,3 tetra(C₁-C₄alkyl)isoindoline

Halogen is fluoro, chloro, bromo or iodo.

The alkyl radicals in the various substituents may be linear or branched. Examples of alkyl containing 1 to 18 carbon atoms are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl and octadecyl.

The alkenyl radicals in the various substituents may be linear or branched. Examples of C₂-C₁₈alkenyl are vinyl, allyl, 2-methylallyl, butenyl, hexenyl, undecenyl and octadecenyl.

Preferred alkenyls are those, wherein the carbon atom in the 1-position is saturated and where the double bond is not activated by substituents like O, C=O, and the like.

Examples of C₂-C₁₈alkynyl are ethynyl, 2-butyne, 3-hexynyl, 5-undecynyl, 6-octadecynyl.

The alkynyl radicals may be linear or branched.

C₇-C₉phenylalkyl is for example benzyl, phenylpropyl, α,α -dimethylbenzyl or α -methylbenzyl.

C₉-C₁₁phenylalkyl is for example α,α -dimethylbenzyl, α,α -metyylethylbenzyl or α,α -diethylbenzyl.

C₃-C₁₂cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C₁-C₄alkyl is typically cyclopropyl, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl.

Alkyl substituted by -OH is typically 2-hydroxyethyl, 2-hydroxypropyl or 2-hydroxybutyl.

C₁-C₁₈Alkyl substituted by C₁-C₈alkoxy, preferably by C₁-C₄alkoxy, in particular by methoxy or ethoxy, is typically 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 3-butoxypropyl, 3-octoxypropyl and 4-methoxybutyl.

C₁-C₁₈Alkyl substituted by di(C₁-C₄alkyl)amino is preferably e.g. dimethylamino, diethylamino, 2-dimethylaminoethyl, 2-diethylaminoethyl, 3-dimethylaminopropyl, 3-diethylaminopropyl, 3-dibutylaminopropyl and 4-diethylaminobutyl.

C₁-C₁₈Alkyl substituted by C₁-C₄alkylamino is preferably e.g. methylamino, ethylamino, 2-methylaminoethyl, 2-ethylaminoethyl, 3-methylaminopropyl, 3-ethylaminopropyl, 3-butylaminopropyl and 4-ethylaminobutyl.

C₁-C₈Alkoxy and, preferably C₁-C₄alkoxy, are typically methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy or octoxy.

C₁-C₄Alkylthio is typically thiomethyl, thioethyl, thiopropyl, thioisopropyl, thiobutyl and thioisobutyl.

C₃-C₁₂cycloalkyl interrupted by at least one nitrogen or oxygen atom is typically oxiran, 1,4-dioxane, tetrahydrofuran, γ -butyrolactone, ϵ -caprolactam, oxirane, aziridine, diaziridine, pyrrole, pyrrolidine, thiophen, furan, pyrazole, imidazole, oxazole, oxazolidine, thiazole, pyran, thiopyran, piperidine or morpholine.

Examples of C₂-C₁₂alkylene bridges, preferably of C₂-C₈alkylene bridges, are ethylene, propylene, butylene, pentylene, hexylene.

C₂-C₁₂alkylene bridges interrupted by at least one N or O atom are, for example,

-CH₂-O-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-CH₂-,
 -CH₂-O-CH₂-CH₂-O-CH₂-, -CH₂-NH-CH₂-CH₂-, -CH₂-NH-CH₂-CH₂-CH₂-,
 -CH₂-NH-CH₂-CH₂-CH₂-CH₂-, -CH₂-NH-CH₂-CH₂-NH-CH₂- or -CH₂-NH-CH₂-CH₂-O-CH₂-.

Examples for C₄-C₁₂cycloalkanone-yl are cyclopentanone-yl, cyclohexanone-yl or cycloheptanone-yl.

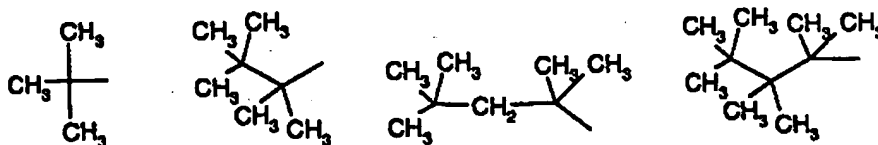
Phenyl substituted by 1, 2 or 3 C₁-C₄alkyl or C₁-C₄alkoxy is typically methylphenyl, dimethylphenyl, trimethylphenyl, t-butylphenyl, di-t-butylphenyl, 3,5-di-t-butyl-4-methylphenyl, methoxyphenyl, ethoxyphenyl and butoxyphenyl.

Examples of polycyclic cycloaliphatic ring systems are adamantane, cubane, twistane, norbornane, bicyclo[2.2.2]octane or bicyclo[3.2.1]octane.

An example of a polycyclic heterocycloaliphatic ring system is hexamethylenetetramine (urotropine).

The C-atom to which the substituents R₁, R₂ and R₃ are bound is preferably a secondary or tertiary C-atom more preferably it is a tertiary C-atom.

Examples for C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom are the following groups:



The monomers suitable for use in the present invention may be water-soluble or water-insoluble. Water soluble monomers contain typically a carboxylic acid group or a salt of a carboxylic acid group. Water insoluble monomers are typically free of acid and phenolic groups.

Typical monoethylenically unsaturated monomers free of carboxylic acid which are suitable for this invention include the alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; the hydroxyalkyl esters of acrylic or methacrylic acids, such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide, methacrylamide, N-tertiary butylacrylamide, N-methylacrylamide, N,N-dimethylacrylamide; acrylonitrile, methacrylonitrile, allyl alcohol, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, phosphoethyl methacrylate, N-vinylpyrrolidone, N-vinylformamide, N-vinylimidazole, vinyl acetate, conjugated dienes such as butadiene or isoprene, styrene, styrenesulfonic acid salts, vinylsulfonic or 2-acrylamido-2-methylpropane-sulfonic acid salts and acryloyl chloride.

The polymerizable composition of the present invention may additionally comprise a solvent selected from the group consisting of water, alcohols, esters, ethers, ketones, amides, sulfoxides, hydrocarbons and halogenated hydrocarbons.

Preferred ethylenically unsaturated monomers or oligomers are selected from the group consisting of styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, (alkyl)acrylic acid anhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters or (alkyl)acrylamides.

Particularly preferred ethylenically unsaturated monomers are styrene, α methyl styrene, p-methyl styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or $\text{C}_1\text{-C}_4$ alkyl, R_b is NH_2 , $\text{O}(\text{Me})$, glycidyl, unsubstituted $\text{C}_1\text{-C}_{18}$ alkoxy or hydroxy-substituted $\text{C}_1\text{-C}_{18}$ alkoxy, unsubstituted $\text{C}_1\text{-C}_{18}$ alkylamino, di($\text{C}_1\text{-C}_{18}$ alkyl)amino, hydroxy-substituted $\text{C}_1\text{-C}_{18}$ alkylamino or hydroxy-substituted di($\text{C}_1\text{-C}_{18}$ alkyl)amino; Me is a monvalent metal atom and Z is oxygen or sulfur.

Typical metal atoms are Na, K or Li.

Examples and preferences for alkyl, alkoxy, alkylamino, dialkylamino and hydroxy-substituted alkoxy are afore mentioned.

In a particular preferred composition R_a is hydrogen or methyl, R_b is NH_2 , glycidyl, unsubstituted or with hydroxy substituted C_1 - C_4 alkoxy, unsubstituted C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, hydroxy-substituted C_1 - C_4 alkylamino or hydroxy-substituted di(C_1 - C_4 alkyl)amino; and Z is oxygen.

Most preferred is a polymerizable composition, wherein the ethylenically unsaturated monomer is methacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, glycidylacrylates, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, glycidyl(meth)acrylates, acrylonitrile, acrylamide or methacrylamide.

Examples of comonomers suitable for use in the present invention are C_3 - C_6 ethylenically unsaturated monocarboxylic acids as well as the alkali metal salts and ammonium salts thereof. The C_3 - C_6 ethylenically unsaturated monocarboxylic acids include acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid and acryloxypropionic acid. Acrylic acid and methacrylic acid are the preferred monoethylenically unsaturated monocarboxylic acid monomers.

Examples for C_8 - C_{18} ethylenically unsaturated phenolics, which may also be used as comonomers include 4-hydroxy styrene, 4-hydroxy, α -methyl styrene, and 2,6-di-tert. butyl, 4-vinyl phenol.

Another class of carboxylic acid monomers suitable for use as comonomers in this invention are C_4 - C_8 ethylenically unsaturated dicarboxylic acids and the alkali metal and ammonium salts thereof as well as the anhydrides of the cis-dicarboxylic acids. Suitable examples include maleic acid, maleic anhydride, itaconic acid, mesaconic acid, fumaric acid and citraconic acid. Maleic anhydride and itaconic acid are the preferred monoethylenically unsaturated dicarboxylic acid monomer(s).

The acid monomers suitable for use in this invention may be in their acid forms or in the form of the alkali metal salts or ammonium salts of the acid. Suitable bases useful for neutralizing

the monomer acids include sodium hydroxide, ammonium hydroxide, potassium hydroxide, and the like. The acid monomers may be neutralized to a level of from 0 to 50% and, preferably, from 0 to about 20%. In many cases, the carboxylic acid monomers may be used in the completely neutralized form. The monomers may be neutralized prior to or during polymerization.

Preferred are neutralized carboxylic acid monomers or anhydrides.

Preferred initiator compounds are those, wherein n is 0 or 1;

R_1 , R_2 , R_3 are each independently of one another NO_2 , cyano, $-(R_9)\text{COOR}_4$, $-\text{CONR}_5R_6$, $-\text{C(O)}-R_7$, $-\text{OR}_8$, carbamoyl, $\text{di}(\text{C}_1\text{-C}_{18}\text{alkyl})\text{carbamoyl}$, $-\text{C(=NR}_5)(\text{NHR}_6)$;

unsubstituted $\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_7\text{-C}_9\text{phenylalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$; or

$\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_7\text{-C}_9\text{phenylalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$, which are substituted by amino, hydroxy, cyano, carboxy, $\text{C}_1\text{-C}_4\text{alkoxy}$, $\text{C}_1\text{-C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$; or

phenyl, which are unsubstituted or substituted by $\text{C}_1\text{-C}_4\text{alkyl}$, $\text{C}_1\text{-C}_4\text{alkoxy}$, $\text{C}_1\text{-C}_4\text{alkylthio}$, halogen, cyano, hydroxy, carboxy, $\text{C}_1\text{-C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$;

or R_2 and R_3 , together with the linking carbon atom, form a $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ radical;

R_4 is, $\text{C}_1\text{-C}_{18}\text{alkyl}$, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R_5 and R_6 are hydrogen, $\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_2\text{-C}_{18}\text{alkyl}$ which is substituted by at least one hydroxy group or, taken together, form a $\text{C}_2\text{-C}_{12}\text{alkylene}$ bridge;

R_7 is hydrogen, $\text{C}_1\text{-C}_{18}\text{alkyl}$ or phenyl;

R_8 is $\text{C}_1\text{-C}_{18}\text{alkyl}$ or $\text{C}_2\text{-C}_{18}\text{alkyl}$ which is substituted by at least one hydroxy group; and

R_9 is $\text{C}_1\text{-C}_4\text{alkyl}$ or a direct bond.

R_{10} is $\text{C}_4\text{-C}_{18}\text{alkyl}$ bound via a tertiary C-atom to the nitrogen atom, phenyl, $\text{C}_9\text{-C}_{11}\text{phenylalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$;

if n is 1

R_{11} is $\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_7\text{-C}_9\text{phenylalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ or

R_{10} and R_{11} together form a $\text{C}_2\text{-C}_{12}\text{alkylene}$ bridge or a $\text{C}_2\text{-C}_{12}\text{alkylene}$ bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with $\text{C}_1\text{-C}_{18}\text{alkyl}$;

R_{12} is, unsubstituted $\text{C}_1\text{-C}_{18}\text{alkyl}$, phenyl, $\text{C}_7\text{-C}_9\text{phenylalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ or

R_{11} and R_{12} together with the linking carbon atom, form a $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ radical.

More preferred are initiators, wherein n is 0 or 1;

R_1 , R_2 , R_3 are each independently of one another NO_2 , cyano, $-(R_9)\text{COOR}_4$, $-\text{CONR}_5R_6$, $-\text{C(O)}-R_7$, $-\text{OR}_8$, carbamoyl, $\text{di}(\text{C}_1\text{-C}_8\text{alkyl})\text{carbamoyl}$, $-\text{C(=NR}_5)(\text{NHR}_6)$;

unsubstituted C₁-C₁₂alkyl, C₇-C₉phenylalkyl or C₅-C₇cycloalkyl; or
 C₁-C₈alkyl, C₇-C₉phenylalkyl or C₅-C₇cycloalkyl or, which are substituted by amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;
 or phenyl,
 or R₂ and R₃, together with the linking carbon atom, form a C₅-C₇ cycloalkyl radical;
 R₄ is C₁-C₈alkyl, phenyl, an alkali metal cation or a tetraalkylammonium cation;
 R₅ and R₆ are hydrogen, C₁-C₈alkyl, C₂-C₈alkyl which is substituted by at least one hydroxy group or, taken together, form a C₂-C₈alkylene bridge;
 R₇ is hydrogen, C₁-C₈alkyl or phenyl;
 R₈ is C₁-C₈alkyl or C₂-C₈alkyl which is substituted by at least one hydroxy group;
 R₉ is C₁-C₄alkylene or a direct bond;
 R₁₀ is C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom or phenyl;
 if n is 1
 R₁₁ is C₁-C₁₈alkyl, phenyl or C₇-C₉phenylalkyl or
 R₁₀ and R₁₁ together form a C₂-C₁₂alkylene bridge or a C₂-C₁₂alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C₁-C₁₈alkyl;
 R₁₂ is unsubstituted C₁-C₁₈alkyl or phenyl.

Particularly preferred initiators are those, wherein n is 0 or 1;

R₁, R₂, R₃ are each independently of one another NO₂, cyano, -C(O)-R₇, -OR₈, unsubstituted C₁-C₁₂alkyl or phenyl, which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;
 or R₂ and R₃, together with the linking carbon atom, form a C₅-C₇ cycloalkyl radical;
 R₇ is, C₁-C₈alkyl or phenyl;
 R₈ is C₁-C₈alkyl or C₂-C₈alkyl which is substituted by at least one hydroxy group and
 R₁₀ is C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, phenyl or C₈-C₁₁phenylalkyl;
 if n is 1
 R₁₁ is C₁-C₁₂alkyl; or
 R₁₀ and R₁₁ together form a C₂-C₈alkylene bridge which is unsubstituted or substituted with C₁-C₄alkyl;
 R₁₂ is hydrogen, unsubstituted C₁-C₄alkyl or phenyl.

Preferably n is 0; R₁ is cyano; R₂ and R₃ are each independently of one another unsubstituted C₁-C₁₂alkyl or phenyl;

or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;
 R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_9 - C_{11} phenylalkyl or phenyl.

Another preferred group is wherein n is 1 R_1 is cyano; R_2 and R_3 are each independently of one another unsubstituted C_1 - C_{12} alkyl or phenyl;

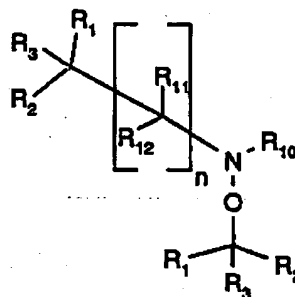
or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;
 R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_9 - C_{11} phenylalkyl or phenyl; or

R_{10} and R_{11} together form a C_2 - C_6 alkylene bridge which is unsubstituted or substituted with C_1 - C_4 alkyl; and

R_{12} is C_1 - C_4 alkyl.

This invention also relates to a free radical polymerization process and polymers obtained thereby, which process overcomes many of the problems and disadvantages of the afore mentioned prior art processes.

This process is used for preparing an oligomer, a cooligomer, a polymer or a copolymer - block or random- by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises (co)polymerizing the monomer or monomers/oli-



gomers in the presence of an initiator compound of formula (I)

(I), under reaction conditions capable of effecting scission of the O-C bond to form two free radicals, the radical $\bullet CR_1R_2R_3$ being capable of initiating polymerization.

Preferably, the scission of the O-C bond is effected by heating, ultrasonic treatment or exposure to actinic radiation.

To perform the scission of the O-C bond by heating, the temperature is particularly preferably raised to more than 50°C and less than 160°C .

The process may be carried out in the presence of an organic solvent or in the presence of water or in mixtures of organic solvents and water. Additional cosolvents or surfactants, such as glycols or ammonium salts of fatty acids, may be present. Other suitable cosolvents are described hereinafter.

Preferred processes use as little solvents as possible. In the reaction mixture it is preferred to use more than 30% by weight of monomer and initiator, particularly preferably more than 50% and most preferably more than 80%.

If organic solvents are used, suitable solvents or mixtures of solvents are typically pure alkanes (hexane, heptane, octane, isooctane), hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons (chlorobenzene), alkanols (methanol, ethanol, ethylene glycol, ethylene glycol monomethyl ether), esters (ethyl acetate, propyl, butyl or hexyl acetate) and ethers (diethyl ether, dibutyl ether, ethylene glycol dimethyl ether), or mixtures thereof.

The aqueous polymerization reactions can be supplemented with a water-miscible or hydrophilic cosolvent to help ensure that the reaction mixture remains a homogeneous single phase throughout the monomer conversion. Any water-soluble or water-miscible cosolvent may be used, as long as the aqueous solvent medium is effective in providing a solvent system which prevents precipitation or phase separation of the reactants or polymer products until after all polymerization reactions have been completed. Exemplary cosolvents useful in the present invention may be selected from the group consisting of aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkyl pyrrolidinones, N-alkyl pyrrolidones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids and salts thereof, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives such as butyl carbitol or cellosolve, amino alcohols, ketones, and the like, as well as derivatives thereof and mixtures thereof. Specific examples include methanol, ethanol, propanol, dioxane, ethylene glycol, propylene glycol, diethylene glycol, glycerol, dipropylene glycol, tetrahydrofuran, and other water-soluble or water-miscible materials, and mixtures thereof. When mixtures of water and water-soluble or water-miscible organic liquids are selected as the aqueous reaction media, the water to cosolvent weight ratio is typically in the range of about 100:0 to about 10:90.

The initiator compound is preferably present in an amount of 0.01 mol-% to 30 mol-%, more preferably in an amount of 0.1 mol-% to 10 mol-% and most preferably in an amount of 0.1 mol-% to 5 mol-%, based on the monomer or monomer mixture used.

When monomer mixtures or monomer/oligomer mixtures are used, the calculation of mol-% is based on an average molecular weight of the mixture.

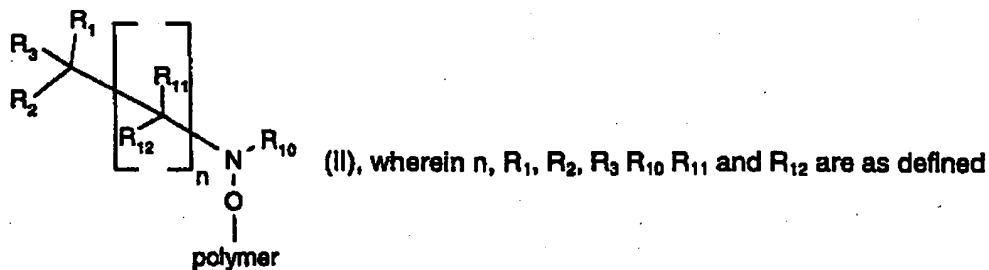
Hydrophilic monomers, polymers and copolymers of the present invention can be separated from one another or from the polymerization reaction mixture by, for example, changing the pH of the reaction media and by other well known conventional separation techniques.

The polymerization temperature may range from about 50°C to about 180°C, preferably from about 80°C to about 150°C. At temperatures above about 180°C, the controlled conversion of the monomer into polymer decreases, and uncertain and undesirable by-products like thermally initiated polymer are formed or destruction of the polymerization regulator may occur. Frequently, these by-products discolor the polymer mixture and a purification step may be required to remove them, or they may be intractable.

Therefore the surprisingly high reactivity of the present initiators which are already active at relatively low temperatures leads to short reaction times. The resulting polymers are usually colourless and they can be used in most cases without any further purification step. This is an important advantage when industrial scale-up is considered.

After the polymerizing step is complete, the formed (co)polymer obtained is isolated. The isolating step of the present process is conducted by known procedures, e.g. by distilling off the unreacted monomer or by precipitation in a suitable nonsolvent, filtering the precipitated polymer followed by washing and drying the polymer.

Yet another embodiment of this invention is a process for preparing a block copolymer involving at least two stages, which comprises forming a polymer with alkoxyamine end groups of the general structure of formula II



above, the polymer containing the initiator group $-CR_1R_2R_3$ and having the oxyamine group

essentially attached as terminal group, and adding a further monomer followed by heating to form a block copolymer.

The homopolymers or copolymers may also be prepared in a so called in "situ process", which means that the compounds of formula (I) are prepared from a radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ and a

compound of formula R_{10}NO or $\text{R}_{12}-\text{C}(\text{R}_{11})=\text{N}^+-\text{R}_{10}$ in the presence of an ethylenically

unsaturated monomer or oligomer. The radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ itself may be prepared as described below, preferably from a compound which liberates the radical upon heating. Under such conditions formation of the compounds of formula (I), their scission and polymerization occur simultaneously. By changing the reaction temperature different pathways of the reaction are favored. It is important to note, that under such reaction conditions still high conversion rates in short reaction times and low polydispersities are achieved.

It is also possible to add the ethylenically unsaturated monomer or oligomer subsequently to

the mixture of a radical initiator and a compound of formula R_{10}NO or $\text{R}_{12}-\text{C}(\text{R}_{11})=\text{N}^+-\text{R}_{10}$. In

this case a compound of formula (I) is prepared to a certain amount, which may be up to 100 % and subsequently the monomer is added without further isolating the compound of formula (I).

Therefore another object of the invention is a process for preparing an oligomer, a co-oligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises generating a free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) from a compound capable of eliminating a neutral molecule, or undergoing C-C bond-scission upon thermal or photochemical treatment, or by hydrogen abstraction from a compound $\text{R}_1\text{R}_2\text{R}_3\text{C-H}$ in reaction with reactive radicals, and

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reacting the free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) with a compound R_{10}NO or

$$\begin{array}{c} \text{R}_{11} \\ | \\ \text{R}_{12}-\text{C}=\text{N}^+-\text{R}_{10} \\ | \\ \text{Q} \end{array}$$

in a

solvent which does not interfere with the radical reaction

in the presence of at least one ethylenically unsaturated monomer or oligomer.

Suitable monomers are those mentioned above. The polymer of formula (II) may be isolated prior to the next reaction step or it may be used without isolation, and the second monomer is added to the reaction mixture of the first step.

Block copolymers are, for example, block copolymers of polystyrene and polyacrylate (e.g., Poly(styrene-co-acrylate) or Poly(styrene-co-acrylate-co-styrene). They are useful as adhesives or as compatibilizers for polymer blends or as polymer toughening agents. Poly(methylmethacrylate-co-acrylate) diblock copolymers or Poly(methylacrylate-co-acrylate-co-methacrylate) triblock copolymers are useful as dispersing agents for coating systems, as coating additives (e.g. rheological agents, compatibilizers, reactive diluents) or as resin component in coatings (e.g. high solid paints). Block copolymers of styrene, (meth)acrylates and/or acrylonitrile are useful plastics, elastomers and adhesives.

Furthermore, block copolymers of this invention, wherein the blocks alternate between polar monomers and non-polar monomers, are useful in many applications as amphiphilic surfactants or dispersants for preparing highly uniform polymer blends.

The (co)polymers of the present invention may have a number average molecular weight from 1 000 to 400 000 g/mol, preferably from 2 000 to 250 000 g/mol and, more preferably, from 2 000 to 200 000 g/mol. When produced in bulk, the number average molecular weight may be up to 500 000 (with the same minimum weights as mentioned above). The number average molecular weight may be determined by size exclusion chromatography (SEC), gel permeation chromatography (GPC), matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) or, if the initiator carries a group which can be easily distinguished from the monomer(s), by NMR spectroscopy or other conventional methods.

The (co)polymers of the present invention typically have a low polydispersity. Preferably the polydispersity is from 1.1 to 2.2, more preferably from 1.1 to 1.9 and most preferably from 1.2 to 1.8.

Thus, the present invention also encompasses in the synthesis novel block, multi-block, star, gradient, random, hyperbranched and dendritic copolymers, as well as graft or copolymers.

The polymers prepared by the present invention are useful for following applications:

adhesives, detergents, dispersants, emulsifiers, surfactants, defoamers, adhesion promoters, corrosion inhibitors, viscosity improvers, lubricants, rheology modifiers, thickeners, crosslinkers, paper treatment, water treatment, electronic materials, paints, coatings, photography, ink materials, imaging materials, superabsorbants, cosmetics, hair products, preservatives, biocide materials or modifiers for asphalt, leather, textiles, ceramics and wood.

Because the present polymerization is a "living" polymerization, it can be started and stopped practically at will. Furthermore, the polymer product retains the functional alkoxyamine group allowing a continuation of the polymerization in a living matter. Thus, in one embodiment of this invention, once the first monomer is consumed in the initial polymerizing step a second monomer can then be added to form a second block on the growing polymer chain in a second polymerization step. Therefore it is possible to carry out additional polymerizations with the same or different monomer(s) to prepare multi-block copolymers.

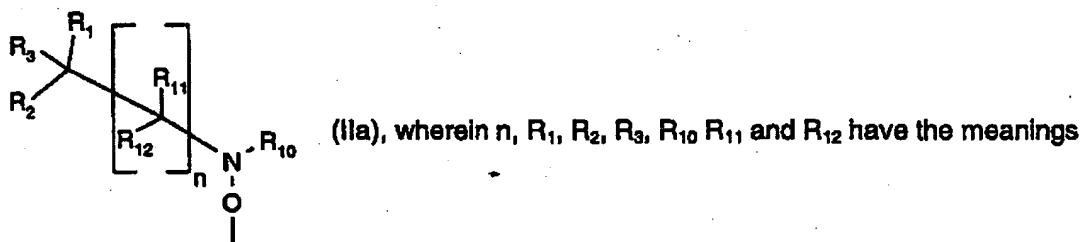
Furthermore, since this is a radical polymerization, blocks can be prepared in essentially any order. One is not necessarily restricted to preparing block copolymers where the sequential polymerizing steps must flow from the least stabilized polymer intermediate to the most stabilized polymer intermediate, such as is the case in ionic polymerization. Thus it is possible to prepare a multi-block copolymer in which a polyacrylonitrile or a poly(meth)acrylate block is prepared first, then a styrene or butadiene block is attached thereto, and so on.

Furthermore, there is no linking group required for joining the different blocks of the present block copolymer. One can simply add successive monomers to form successive blocks.

A plurality of specifically designed polymers and copolymers are accessible by the present invention, such as star and graft (co)polymers as described, inter alia, by C. J. Hawker in *Angew. Chemie*, 1995, 107, pages 1623-1627, dendrimers as described by K. Matyaszewski et al. in *Macromolecules* 1996, Vol 29, No. 12, pages 4167-4171, graft (co)polymers as described by C. J. Hawker et al. in *Macromol. Chem. Phys.* 198, 155-166(1997), random copolymers as described by C. J. Hawker in *Macromolecules* 1996, 29, 2686-2688, or

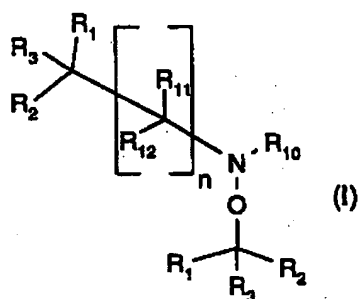
diblock and triblock copolymers as described by N. A. Listigovers in *Macromolecules* 1996, 29, 8992-8993.

Yet another object of the present invention is a polymer or oligomer, having at least one initiator group $-CR_1R_2R_3$ and at least one oxyamine group of formula (IIa)



and preferred meanings as defined above, obtainable by the process as defined above.

In another of its aspects, this invention relates to a compound of formula (I)



wherein n is 0 or 1


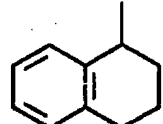
R_1 , R_2 , R_3 are each independently of one another hydrogen, halogen, NO_2 , cyano, $-CONR_5R_6$, $-(R_9)COOR_4$, $-C(O)-R_7$, $-OR_8$, $-SR_8$, $-NHR_8$, $-N(R_9)_2$, carbamoyl, di(C_1 - C_{18} alkyl)carbamoyl, $-C(=NR_5)(NHR_6)$;

unsubstituted C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or di(C_1 - C_4 alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or di(C_1 - C_4 alkyl)amino;

or R_2 and R_3 , together with the linking carbon atom, form a C_3 - C_{12} cycloalkyl radical, a (C_4 - C_{12} cycloalkanon)-yl radical or a C_3 - C_{12} cycloalkyl radical containing at least one O atom

and/or a NR_8 group; or if n is 1 R_2  are a group  ;

R_4 is hydrogen, C_1 - C_{18} alkyl, phenyl, an alkali metal cation or a tetraalkylammonium cation;
 R_5 and R_6 are hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is substituted by at least one hydroxy group or, taken together, form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} -alkylene bridge interrupted by at least one O or/and NR_8 atom;

R_7 is hydrogen, C_1 - C_{18} alkyl or phenyl;

R_8 is hydrogen, C_1 - C_{18} alkyl or C_2 - C_{18} alkyl which is substituted by at least one hydroxy group;

R_9 is C_1 - C_{12} alkylene or a direct bond;

R_{10} is C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, C_9 - C_{11} phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, C_9 - C_{11} phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom;

If n is 1

R_{11} is C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R_{10} and R_{11} together form a C_2 - C_{12} alkylene bridge, a C_3 - C_{12} alkylen-on bridge or a C_2 - C_{12} alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C_1 - C_{18} alkyl, hydroxy(C_1 - C_4)alkyl, phenyl, C_7 - C_9 phenylalkyl,

NO_2 , halogen, amino, hydroxy, cyano, carboxy, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ alkylamino or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$, or

R_{12} is hydrogen, $-(\text{R}_8)\text{COOR}_4$, cyano, $-\text{OR}_8$, $-\text{SR}_8$, $-\text{NHR}_8$, $-\text{N}(\text{R}_8)_2$, $-\text{NH-C(O)-R}_8$, unsubstituted $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_2\text{-C}_{18}$ alkenyl, $\text{C}_2\text{-C}_{18}$ alkynyl, $\text{C}_7\text{-C}_9$ phenylalkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl or $\text{C}_3\text{-C}_{12}$ cycloalkyl containing at least one nitrogen or oxygen atom; or

$\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_2\text{-C}_{18}$ alkenyl, $\text{C}_2\text{-C}_{18}$ alkynyl, $\text{C}_7\text{-C}_9$ phenylalkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl or $\text{C}_3\text{-C}_{12}$ cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 ,

halogen, amino, hydroxy, cyano, carboxy, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ alkylamino or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$; or

phenyl, naphthyl, which are unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylthio, halogen, cyano, hydroxy, carboxy, $\text{C}_1\text{-C}_4$ alkylamino, $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$; or

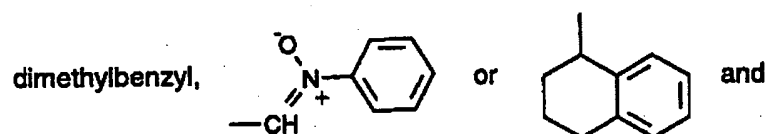
R_{11} and R_{12} together with the linking carbon atom, form a $\text{C}_3\text{-C}_{12}$ cycloalkyl radical;

with the proviso that

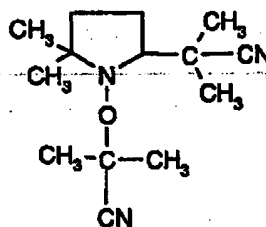
if n is 0 R_{10} is different from the group $-\text{CR}_1\text{R}_2\text{R}_3$, and if R_1 is CN and R_2 and R_3 are methyl, R_{10} is not phenyl, phenyl substituted by methyl, 2,4,6-trimethyl, chlor, fluor, (3-methyl,4-fluor), (3-fluor, 4-methyl), (4-fluor, 2-methyl), (4-fluor, 2-methoxy), (2-fluor, 3,5-methyl), 2,5-di-tert.butyl, nitro, 3,5-dinitro or 2 $(-\text{O-C}(\text{CH}_3)_2\text{CN})$ 4-nitro; and

if n is 1, R_{12} is hydrogen, R_{10} phenyl or benzyl and R_{11} phenyl,

R_1 , R_2 and R_3 are not a group $-\text{C}(\text{CH}_3)_2\text{CN}$, $-\text{C}(\text{CH}_3)_2\text{COOCH}_3$, benzyl, methylbenzyl,



the compound according to formula I is not



Preferred compounds are those wherein n is 0 or 1;

R_1 , R_2 , R_3 are each independently of one another NO_2 , cyano, $-\text{C(O)-R}_7$, $-\text{OR}_8$, unsubstituted $\text{C}_1\text{-C}_{12}$ alkyl or phenyl, which is unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, cyano, hydroxy, carboxy, $\text{C}_1\text{-C}_4$ alkylamino or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$;

or R_2 and R_3 , together with the linking carbon atom, form a $\text{C}_5\text{-C}_7$ cycloalkyl radical;

R_7 is, $\text{C}_1\text{-C}_8$ alkyl or phenyl;

R_8 is C_1 - C_8 alkyl or C_2 - C_8 alkyl which is substituted by at least one hydroxy group and

R_{10} is C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, phenyl or C_8 -

C_{11} phenylalkyl;

if n is 1

R_{11} is C_1 - C_{18} alkyl, C_7 - C_8 phenylalkyl or C_3 - C_{12} cycloalkyl or

R_{10} and R_{11} together form a C_2 - C_6 alkylene bridge which is unsubstituted or substituted with

C_1 - C_4 alkyl;

R_{12} is , unsubstituted C_1 - C_4 alkyl or phenyl.

Particularly preferred are compounds wherein n is 0;

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1 - C_{12} alkyl or phenyl;

or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;

R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom or C_8 - C_{11} phenylalkyl.

Another particularly preferred group of compounds are those wherein n is 1;

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1 - C_{12} alkyl or phenyl;

or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;

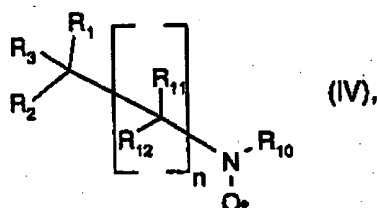
R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_8 - C_{11} phenylalkyl or phenyl; or

R_{10} and R_{11} together form a C_2 - C_6 alkylene bridge which is unsubstituted or substituted with C_1 - C_4 alkyl; and

R_{12} is C_1 - C_4 alkyl.

Further meanings and preferences for the different substituents R_1 to R_{12} are mentioned before.

The invention is also directed to a compound of formula (IV)



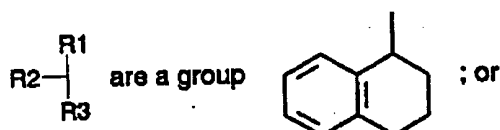
wherein n is 0 or 1

R_1, R_2, R_3 are each independently of one another hydrogen, halogen, NO_2 , cyano, $-\text{CONR}_5\text{R}_6$, $-(\text{R}_9)\text{COOR}_4$, $-\text{C}(\text{O})-\text{R}_7$, $-\text{OR}_8$, $-\text{SR}_8$, $-\text{NHR}_8$, $-\text{N}(\text{R}_8)_2$, carbamoyl, $\text{di}(\text{C}_1-\text{C}_{18}\text{alkyl})\text{carbamoyl}$, $-\text{C}(=\text{NR}_5)(\text{NHR}_6)$;

unsubstituted $\text{C}_1-\text{C}_{18}\text{alkyl}$, $\text{C}_2-\text{C}_{18}\text{alkenyl}$, $\text{C}_2-\text{C}_{18}\text{alkynyl}$, $\text{C}_7-\text{C}_9\text{phenylalkyl}$, $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ or $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom; or

$\text{C}_1-\text{C}_{18}\text{alkyl}$, $\text{C}_2-\text{C}_{18}\text{alkenyl}$, $\text{C}_2-\text{C}_{18}\text{alkynyl}$, $\text{C}_7-\text{C}_9\text{phenylalkyl}$, $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ or $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylthio}$, $\text{C}_1-\text{C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1-\text{C}_4\text{alkyl})\text{amino}$; or

phenyl, naphthyl, which are unsubstituted or substituted by $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylthio}$, halogen, cyano, hydroxy, carboxy, $\text{C}_1-\text{C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1-\text{C}_4\text{alkyl})\text{amino}$; or R_2 and R_3 , together with the linking carbon atom, form a $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ radical, a $(\text{C}_4-\text{C}_{12}\text{cycloalkanon})\text{-yl}$ radical or a $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ radical containing at least one O atom and/or a NR_8 group; or if n is 1



R_4 is hydrogen, $\text{C}_1-\text{C}_{18}\text{alkyl}$, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R_5 and R_6 are hydrogen, $\text{C}_1-\text{C}_{18}\text{alkyl}$, $\text{C}_2-\text{C}_{18}\text{alkyl}$ which is substituted by at least one hydroxy group or, taken together, form a $\text{C}_2-\text{C}_{12}\text{alkylene}$ bridge or a $\text{C}_2-\text{C}_{12}\text{alkylene}$ bridge interrupted by at least one O or/and NR_8 atom;

R_7 is hydrogen, $\text{C}_1-\text{C}_{18}\text{alkyl}$ or phenyl;

R_8 is hydrogen, $\text{C}_1-\text{C}_{18}\text{alkyl}$ or $\text{C}_2-\text{C}_{18}\text{alkyl}$ which is substituted by at least one hydroxy group;

R_9 is $\text{C}_1-\text{C}_{12}\text{alkylene}$ or a direct bond;

R_{10} is $\text{C}_4-\text{C}_{18}\text{alkyl}$ bound via a tertiary C-atom to the nitrogen atom, $\text{C}_6-\text{C}_{11}\text{phenylalkyl}$, $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ or $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom; or $\text{C}_4-\text{C}_{18}\text{alkyl}$ bound via a tertiary C-atom to the nitrogen atom, $\text{C}_6-\text{C}_{11}\text{phenylalkyl}$, $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ or $\text{C}_3-\text{C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom, which are

substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom;

if n is 1

R₁₁ is C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R₁₀ and R₁₁ together form a C₂-C₁₂alkylene bridge, a C₃-C₁₂alkylen-on bridge or a C₂-C₁₂alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C₁-C₁₈alkyl, hydroxy(C₁-C₄)alkyl, phenyl, C₇-C₉phenylalkyl, NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;

R₁₂ is hydrogen, -(R₈)COOR₈, cyano, -OR₈, -SR₈, -NHR₈, -N(R₈)₂, -NH-C(O)-R₈, unsubstituted C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino; or

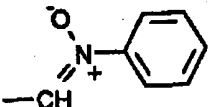
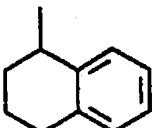
R₁₁ and R₁₂ together with the linking carbon atom, form a C₃-C₁₂ cycloalkyl radical; with the proviso that

if n is 0 R₁₀ is different from the group -CR₁R₂R₃, and if R₁ is CN and R₂ and R₃ are methyl, R₁₀ is not phenyl, phenyl substituted by methyl, 2,4,6-trimethyl, chlor, fluor, (3-methyl,4-fluor),

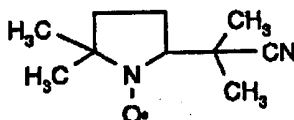
(3-fluor, 4-methyl), (4-fluor, 2-methyl), (4-fluor, 2-methoxy), (2-fluor, 3,5-methyl), 2,5-di-tert-butyl, nitro, 3,5-dinitro or 2 (-O-C(CH₃)₂CN) 4-nitro; and

if n is 1, R₁₂ is hydrogen, R₁₀ phenyl or benzyl and R₁₁ phenyl,

R₁, R₂ and R₃ are not a group -C(CH₃)₂CN, -C(CH₃)₂COOCH₃, benzyl, methylbenzyl,

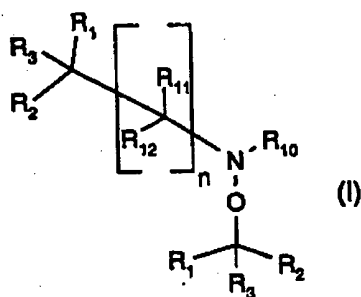
dimethylbenzyl,  or  and

the compound according to formula IV is not

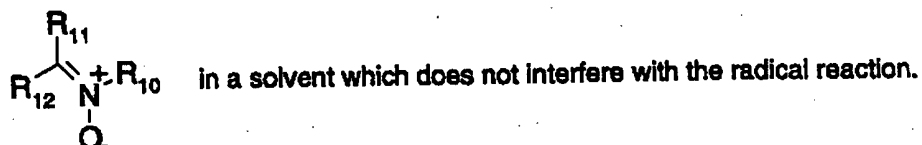


Meanings and preferences for the different substituents R₁ to R₁₂ are already mentioned.

A further object of the present invention is a process for preparing a compound of formula (I)



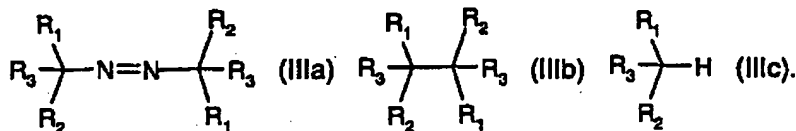
by generating a free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) from a compound capable of eliminating a neutral molecule, or undergoing C-C bond-scission upon thermal or photochemical treatment, or by hydrogen abstraction from a compound R₁R₂R₃C-H in reaction with reactive radicals, and reacting the free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) with a compound of formula R₁₀NO or



Examples for neutral molecules which can be eliminated are N_2 or O_2 . Reactive radicals which are able to abstract hydrogen are for example alkoxy radicals.

Suitable solvents are aromatic, aliphatic or cycloaliphatic hydrocarbons, such as toluene, benzene xylene, octane or cyclohexane, ethers, such as dioxane, tetrahydrofuran or dibutylether, alcohols, glycols or esters and amides of carboxylic acids.

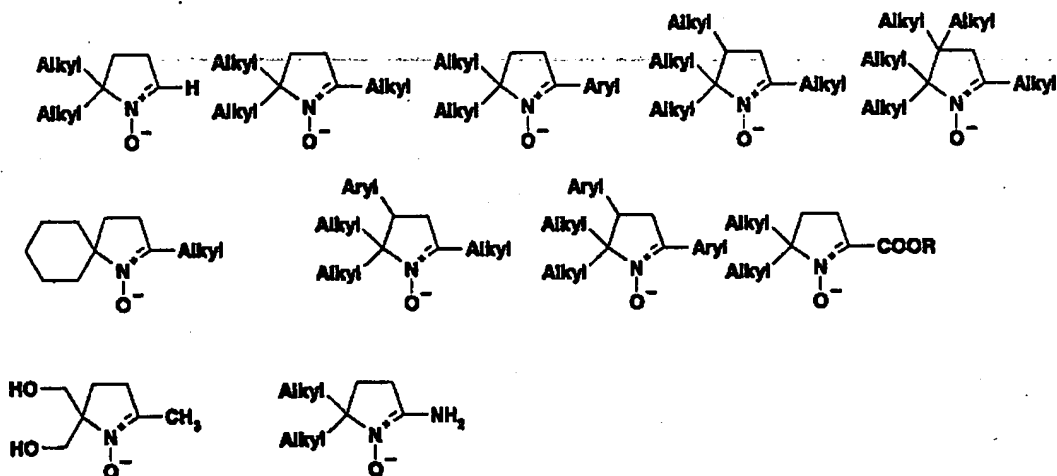
The free radical $\bullet CR_1R_2R_3$ is preferably prepared by heating or irradiation of a compound of formula IIIa, IIIb or IIIc



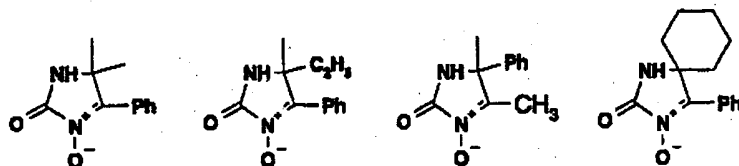
Preferably the radical $\bullet CR_1R_2R_3$ is prepared by a thermal reaction at a temperature from 40° to 150° C, more preferably from 60° to 150° C and most preferably from 70° to 140° C. R_1 , R_2 and R_3 have the meanings and preferred meanings defined above.

Nitrones of formula (VI) can be prepared according to known methods.

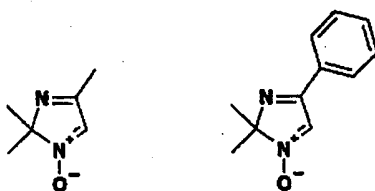
Examples of 5-membered nitrones are for example described by J.B. Bapat and D.St. C. Black in Aust. J. Chem. 21, 2483 (1968). Typical examples are mentioned below.



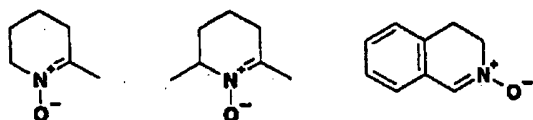
Further nitrones are described by H. Gnichtel, K.E. Schuster in Chem. Ber. 111, 1171 (1978).



A. G. Krainev, T.D. Williams, D. J. Bigelow describe in J. Magnet. Res., B 111, 272 (1996) the preparation of following nitrones.



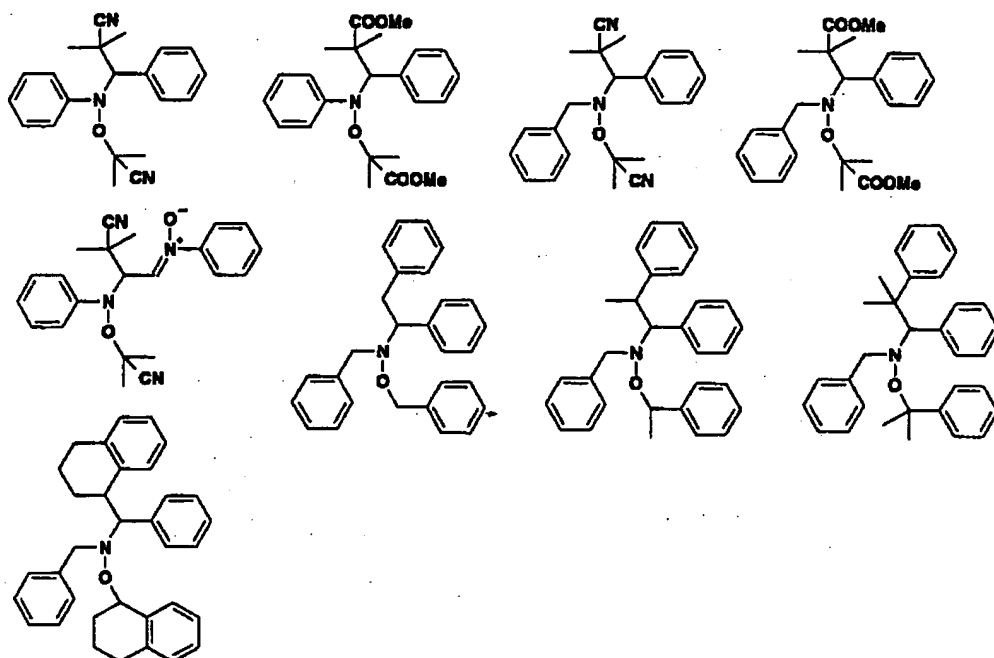
Examples of 6-membered nitrones are for example described by Shun-Ishi Murahashi et al. in J. Org. Chem. 55, 1736 (1990).



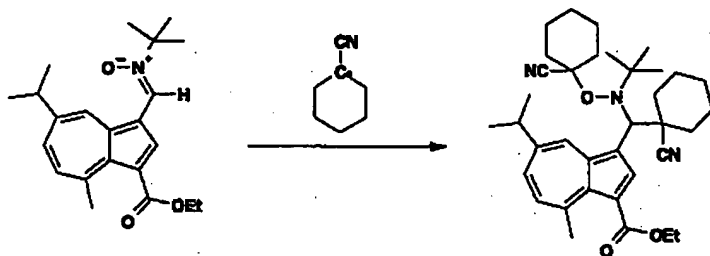
These nitrones may be reacted with the appropriate reactive radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ to obtain compounds of formula (I).

Some reaction products between nitrones and reactive radicals have been reported and are listed below.

M. Iwamura, N. Inamoto: Bull. Chem. Soc. Japan 43, 856 (1970):



or D.A. Becker: J.Am. Chem. Soc. 118, 905 (1996).



M. Iwamura, N. Inamoto: Bull. Chem. Soc. Japan 43, 860 (1970) have reported the preparation of the following compound.



None of these compounds have been used to polymerize ethylenically unsaturated monomers or oligomers.

The production of C-centered radicals is described, inter alia, in Houben Weyl, Methoden der Organischen Chemie, Vol. E 19a, pages 60-147. These methods can be applied in general analogy.

The reaction of reacting radicals with nitroso compounds is known per se and described by B. A. Gingras et al. in J. Chem. Soc. page 1920, 1954.

Most preferably, the free radical source is 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobis(isobutyramide) dihydrate, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, dimethyl-2,2'-azobisisobutyrate, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), 2,2'-azobis(N,N'-dimethyleneisobutyramidine), free base or hydrochloride, 2,2'-azobis(2-amidinopropane), free base or hydrochloride, 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide) or 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide).

These compounds are commercially available.

If more than one radical source is used, a mixture of substitution patterns is obtainable.

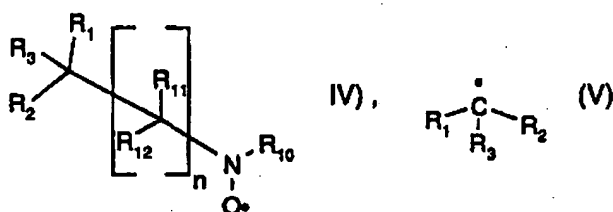
This invention also relates to the use of an Initiator compound of formula (I) for polymerizing ethylenically unsaturated monomers.

The alkoxyamines of formula (I) may be prepared and isolated as described above.

However, it is also possible to produce the compounds of formula (I) in situ during polymerization by adding a compound of formula IV, which has been isolated as intermediate in the process described before, to the polymerizable monomers and by adding, also in situ, the corresponding radical initiator.

Consequently a further aspect of the invention is a polymerizable composition, comprising

- a) at least one ethylenically unsaturated monomer or oligomer;
- b) a compound of formula (IV) and
- c) a radical initiator as described above capable of generating a free radical of formula (V)



wherein n , R_1 , R_2 , R_3 , R_{10} , R_{11} and R_{12} are as defined above including their preferences.

Still another aspect of the invention is a process for preparing an oligomer, a cooligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer/oligomer, which comprises subjecting a composition as described above to heat or actinic radiation.

A further aspect of the present invention is the use of a compound of formula I for polymerizing ethylenically unsaturated monomers.

Suitable initiators are those listed above including their preferences.

The following Examples illustrate the invention in more detail.

A) Examples for the preparation of N,N,O-trisubstituted hydroxylamines (table 1)

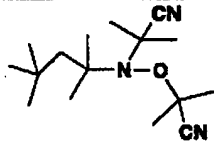
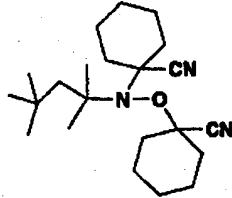
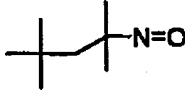
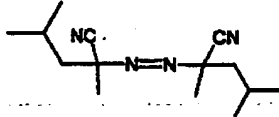
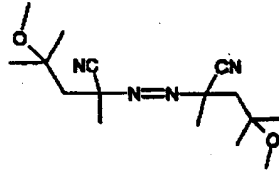
Example A1. Preparation of N-(1,1,3,3-tetramethyl-butyl)-N,O-bis-(1-cyano-1-methyl-ethyl)-hydroxylamin compound (101).

8,6 g (0,06 mol) 1-nitroso-1,1,3,3-tetramethyl-butan (prepared according to Org. Synth. 65, 166 (1986)) and 24,9 g (0,15 mol) azobis-isobutyronitril are dissolved in 100 ml benzene. After careful purge with argon the solution is refluxed for 2 hours under argon atmosphere. Benzene is distilled off on the rotary evaporator and the residue is diluted with 100 ml hexane. The precipitated 2,3-dimethyl-succinicacid dinitrile was removed by filtration. The filtrate is evaporated and subjected to column chromatography on silica gel (hexane - ethylacetate 9:1). 14,8 g (88%) of the compound of formula (101) are obtained as viscous oil.

Example A2. Preparation of N-(1,1,3,3-tetramethyl-butyl)-N,O-bis-(1-cyano-cyclohexyl)-hydroxylamin (102).

1,4 g (0,01 Mol) 1-nitroso-1,1,3,3-tetramethyl-butan and 4,9 g (0,02 Mol) azobis-(1-cyanocyclohexane) are dissolved in 25 ml chlorbenzene. After careful purge with argon the solution is heated to 100° C for 3 hours under argon atmosphere. Chlorbenzene is distilled off on the rotary evaporator. The residue subjected to column chromatography on silica gel (hexane / ethylacetate 9:1) and recrystallized from hexane. 1.45 g (39%) of the compound of formula (102) are obtained.

Table 1

Nr.	compound	mp. (°C)	C(%), H(%), N(%) calc. / found
101		viscous oil	68,78; 10,46; 15,04 / 68,79; 10,34; 15,04
102		108-112	73,49; 10,37; 11,69 / 73,39; 10,43; 11,66
104			
V-65			
V-70			

Example A3. Preparation of 1-(1-cyano-1-methyl-ethoxy)-2-(1-cyano-1-methyl-ethyl)-2,5,5-tetra-methyl-pyrrolidin (105).

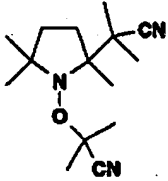
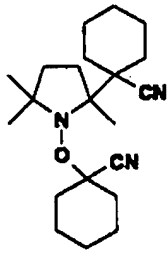
16 g (0.125 Mol) 2,5,5-trimethyl-pyrrolin-1-oxid [prepared according to M.J. Turner et al.: Synth. Commun. **16** (11), 1377 (1986)] and 37 g (0.225 Mol) azobis-isobutyronitril are

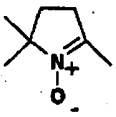
dissolved in 150 ml benzene. After careful purge with argon the solution is refluxed for 6 hours under argon atmosphere. Benzene is distilled off on the rotary evaporator and the residue is diluted with 100 ml hexane. The precipitated 2,3-dimethyl-succinicacid dinitrile was removed by filtration. The filtrate is evaporated and subjected to column chromatography on silica gel (hexane / ethylacetate 9:1). 9,6 g (29%) of the compound of formula (101) are obtained, m.p. 65-69° C

Example A4: Preparation of 1-(1-cyano-cyclohexyloxy)-2-(1-cyano-cyclohexyl)-2,4,4-tetra-methyl-pyrrolidin (106).

7.65 g (0.06 Mol) 2,4,4-trimethyl-pyrrolin-1-oxid [prepared according to M.J. Turner et al.: Synth. Commun. **16** (11), 1377 (1986)] and 22 g (0.09 Mol) azobis-(1-cyanocyclohexan) are dissolved in 75 ml chlorbenzene. After careful purge with argon the solution is heated to 100° C for 8,5 hours under argon atmosphere. Chlorbenzene is distilled off on the rotary evaporator. The residue subjected to column chromatography on silica gel (hexane / ethylacetate 9:1) and recrystallized from dichlormethane/hexane. 10,1 g (49%) of the compound of formula (102) are obtained, m.p. 124°-127° C.

Table 2

Nr.	Compound	m.p. (°C)	C(%), H(%), N(%) Ber. / Gef.
105		65 - 69	68.40 9.57 15.95 68.34 9.47 15.91
106		124 - 127	73.43 9.68 12.23 73.27 9.26 12.23

107			
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Compounds V-65 and V-70 (WACO) are commercially available.

B) Polymerizations using compounds of Table 1 and Table 2 as initiators

General remarks:

Solvents and monomers are distilled over a Vigreux column under argon atmosphere or under vacuum, shortly before being used.

To remove oxygen all polymerization reaction mixtures are flushed before polymerization with argon and evacuated under vacuum applying a freeze-thaw cycle. The reaction mixtures are then polymerized under argon atmosphere.

At the start of the polymerization reaction, all starting materials are homogeneously dissolved.

Conversion is determined by removing unreacted monomers from the polymer at 80° C and 0.002 torr for 30 minutes, weighing the remaining polymer and subtract the weight of the initiator.

Characterization of the polymers is carried out by MALDI-MS (Matrix Assisted Laser Desorption Ionization Mass Spectrometry) and/or GPC (Gel Permeation Chromatography).

MALDI-MS: Measurements are performed on a linear TOF (Time Of Flight) MALDI-MS LDI-1700 Linear Scientific Inc., Reno, USA. The matrix is 2,5-dihydroxybenzoic acid and the laser wavelength is 337 nm.

GPC: Is performed using RHEOS 4000 of FLUX INSTRUMENTS. Tetrahydrofurane (THF) is used as a solvent and is pumped at 1 ml/min. Two chromatography columns are put in series: type Plgel 5µm mixed-C of POLYMER INSTRUMENTS, Shropshire, UK.

Measurements are performed at 40 °C. The columns are calibrated with low polydispersity

polystyrenes having Mn from 200 to 2 000 000 Dalton. Detection is carried out using a RI-Detector ERC-7515A of ERCATECH AG at 30 °C.

Example B1. Polymerization of n-butylacrylate using compound 101

In a 50 ml three neck flask, equipped with thermometer, cooler and magnetic stirrer, 654 mg (2.34 mmol) of compound 101 and 20 g (156 mmol) of n-butylacrylate are mixed and degased. The clear solution obtained is heated under argon to 120 °C. Polymerization starts spontaneously and the temperature rises to 143° C. After 15 minutes, the exothermal reaction slowly stops and the viscosity of the solution increases. The reaction mixture is stirred for an additional 10 minutes at 145 °C and is then cooled to 80 °C. The remaining monomer is removed by evaporation under high vacuum. 19.1 g (95%) of the initial monomer have reacted. A clear colourless viscous fluid is obtained.

MALDI-MS : Mn = 3400, Mw = 6100, PD = 1.8

Example B2. Polymerization of n-butylacrylate using compound 102 in xylene

In a 100 ml three neck flask, equipped with thermometer, cooler and magnetic stirrer, 841 mg (2.34 mmol) of compound 102, 20 g (156 mmol) of n-butylacrylate and 10 g xylene are mixed and degased. The clear solution obtained is heated under argon to 130 °C. Polymerization starts spontaneously and the temperature rises to 141° C. After 10 minutes, the exothermal reaction slowly stops. The reaction mixture is then cooled to room temperature. The remaining monomer and solvent is removed by evaporation at 80° C under high vacuum. 18.1 g (87%) of the initial monomer have reacted. A clear colourless viscous fluid is obtained.

GPC : Mn = 7400, Mw = 14800, PD = 2

Example B3. Polymerization of n-butylacrylate using compound 101 in octane.

In a 50 ml three neck flask, equipped with thermometer, cooler and magnetic stirrer, 279 mg (1.75 mmol) of compound 101 and 15 g (117 mmol) of n-butylacrylate in 7.5g octane are mixed and degased. The clear solution obtained is heated under argon to 130 °C. Polymerization starts spontaneously. After 15 minutes, the exothermal reaction slowly stops and the viscosity of the solution increases. The reaction mixture is stirred for an additional 2.5h at 130 °C and is then cooled to 80 °C. The remaining monomer is removed by evaporation under high vacuum. 14.0 g (93%) of the initial monomer have reacted. A clear colorless viscous fluid is obtained.

GPC analysis: Mn 8500, Mw: 15300, Polydispersity (PD): 1.8

Example B4. Polymerization of n-butylacrylate using compound 102 in toluene.

631 mg (1.8 mmol) of compound 102, 15 g (117 mmol) n-butylacrylate and 7.5 g toluene are reacted at 110 °C for 2.5 h. After evaporation of volatile components 14.8 g (95%) polymer are obtained.

GPC : $M_n = 7100$, $M_w = 13200$, $PD = 1.8$

Example B5. Polymerization of n-butylacrylate using compound 102 in heptane.

1.4 g (3.9 mmol) of compound 102, 5 g (39 mmol) n-butylacrylate and 2.5 g heptane are reacted at 100 °C for 22 h. After evaporation of volatile components 5.9 g (91%) of viscous liquid are obtained.

GPC : $M_n = 1300$, $M_w = 2100$, $PD = 1.6$

Example B6. Polymerization of methylmethacrylate (MMA) using compound 102 in toluene.

808 mg (2.25 mmol) of compound 102, 15 g (150 mmol) MMA and 7.5 g toluene are reacted at 110 °C for 2.5 h. After evaporation of volatile components 9.2 g (61%) of a solid white foam are obtained.

GPC : $M_n = 3000$, $M_w = 5800$, $PD = 1.9$

Example B7. Polymerization of methacrylic acid -2-diamino-ethylester (MADMAEE) using compound 102 in heptane.

686 mg (1.91 mmol) of compound 102, 20 g (127 mmol) MADMAEE and 10 g heptane are reacted at 100 °C for 5 h. After evaporation of volatile components 13.1 g (66%) of a partially solid material are obtained.

GPC : $M_n = 4300$, $M_w = 7400$, $PD = 1.7$

Example B8. Polymerization of methacrylic acid-glycidylester (MAGE) using compound 102 in dioxane.

1.52 g (4.22 mmol) of compound 102, 20 g (141 mmol) MAGE and 10 g dioxane are reacted at 100 °C for 1 h. After evaporation of volatile components 13.9 g (62%) of a viscous material are obtained.

GPC : Mn = 3800, Mw = 6100, PD = 1.6

Example B9. Polymerization of acrylic acid-4-hydroxybutylester using compound 102 in dioxane.

1.66 g (4.6 mmol) of compound 102, 22.2 g (154 mmol) of acrylic acid-4-hydroxybutylester and 11.1 g dioxane are reacted at 105 °C for 2.5 h. After evaporation of volatile components 20.1 g (83%) of a viscous material are obtained.

GPC : Mn = 4000, Mw = 7100, PD = 1.8

Example B10. Polymerization of acrylic acid-(3-sulfopropylester) Kallum-salt using compound 102.

0.232 g (0.65mmol) of compound 102, 10 g (43 mmol) acrylic acid-(3-sulfopropylester) Kallum-salt, 90 g ethylenglykol and 10 g water are mixed, degassed and heated to 90 °C. The mixture is reacted for 20 h. The clear polymer solution is poured into acetone. The white solid polymer is filtered off and dried under high vacuum. 5.8 g (56%) are obtained. ¹H-NMR in D₂O shows no acrylate double bond between 6-6.5 ppm, thus indicating that all monomer has reacted.

Example B11. Random copolymer from n-butylacrylate and methacrylic acid -2-diamino ethylester (MADMAEE) using compound 102.

1.37 g (3.81 mmol) of compound 102, 16.3 g (127 mmol) of n-butylacrylate, 20 g (127mmol) of MADMAEE and 18 g octane are reacted at 130 °C for 2.5 h. After evaporation of volatile components 30.7 g (85%) copolymer are obtained.

GPC : Mn = 5300, Mw = 9200, PD = 1.7

Example B12. Random copolymer from n-butylacrylate and methylmethacrylate using compound 102.

2.17 g (6.03 mmol) of compound 102, 7 g (70.3 mmol) methylmethacrylate and 10 g (70.3 mmol) of n-butylacrylate in 8.5 g dioxane are degassed and reacted at 105 °C for 5 h under argon. After evaporation of volatile components 15 g (75%) copolymer are obtained.

GPC : Mn = 2200, Mw = 3800, PD = 1.7

Example B13. Blockcopolymer from n-butylacrylate and acrylic acid-2-ethoxyethylester

3 g (8.34 mmol) of compound 102, 17.8 g (139 mmol) n-butylacrylate and 9 g toluene are reacted at 115 °C for 2,5 h. After evaporation of volatile components 13.9 g (61%) polymer are obtained. 20 g (139 mmol) acrylic acid-2-ethoxyethylester and 19 g toluene are added. The mixture is reacted at 115 °C for 2,5 h. After evaporation of volatile components 33.4 g (98% , based on the second monomer) copolymer are obtained. Total conversion is 60%.

GPC : Mn = 3900, Mw = 7800, PD = 2

Example B14. Blockcopolymer from n-butylacrylate and acrylic acid-3-hydroxypropylester

3 g (8.34 mmol) of compound 102, 17.8 g (139 mmol) n-butylacrylate and 9 g dioxane are reacted at 105 °C for 2,5 h. After evaporation of volatile components 15.2 g (69%) polymer are obtained. 18.1 g (139 mmol) acrylic acid-3-hydroxypropylester and 18 g dioxane are added. The mixture is reacted at 105 °C for 2 h. After evaporation of volatile components 33.8 g (100% , based on the second monomer) copolymer are obtained. Total conversion is 69%.

GPC : Mn = 3300, Mw = 11500, PD = 3.5

Example B15. Blockcopolymer from n-butylacrylate and acrylic acid

1.85 g (5.1 mmol) of compound 102, 20 g (156 mmol) n-butylacrylate and 10 g octane are reacted at 130 °C for 2,5 h. After evaporation of volatile components 21.3 g (97%) polymer are obtained. 1.12 g (15.6 mmol) acrylic acid and 11 g dioxane are added. The mixture is reacted at 105 °C for 2.5 h. After evaporation of volatile components 22.3 g (89% , based on the second monomer) copolymer are obtained.

GPC : Mn = 4200, Mw = 6500, PD = 1.6

Example B16. Blockcopolymer from n-butylacrylate and methylmethacrylate

3.08 g (8.58 mmol) of compound 102, 20 g (156 mmol) n-butylacrylate and 10 g octane are reacted at 130 °C for 2,5 h. After evaporation of volatile components 22.7 g (98%) polymer are obtained. 15.6 g (156 mmol) methylmethacrylate and 10 g octane are added. The mixture is reacted at 130 °C for 2.5 h. After evaporation of volatile components 29.4 g copolymer are obtained. Total conversion is 43%.

GPC : $M_n = 2800$, $M_w = 3900$, $PD = 1.5$

Example B17. Blockcopolymer from n-butylacrylate and methacrylic acid-2-dimethylamino-ethyl ester (MADMAEE)

1.37 g (3.81 mmol) 102, 16.3 g (127 mmol) n-butylacrylate and 18 g octane are reacted at 130 °C for 2.5 h. Volatile components are evaporated and 20 g (127 mmol) MADMAEE in 18 g octane are added and reacted at 130 °C for 2.5 h. After evaporation of volatile components 30.3 g (80%) of blockcopolymer are obtained.

GPC : $M_n = 4800$, $M_w = 9700$, $PD = 2$

Example B18. Homopolymerization of styrene using compound 102

In a 50 ml flask 0.719 g (2 mmol) of compound 102, 20.9 g (200 mmol) styrene and 20 g toluene are mixed. The mixture is refluxed and polymerized for 6 h. After evaporation of volatile components 9.73 g (47 %) polymer are obtained.

GPC : $M_n = 3100$, $M_w = 4900$, $PD = 1.6$

Example B19. In situ preparation of Initiator from compound 104 and azobisisobutyronitrile and simultaneous polymerization of n-butylacrylate

0.447 g (3.12 mmol) 104, 0.512 g (3.12 mmol) azobisisobutyronitrile (AIBN), 20 g (156 mmol) n-butylacrylate and 10 g octane are mixed in a 100 ml flask and degassed. The mixture is reacted at 80 °C for 2 h under stirring. Temperature is slowly raised to 130 °C. Polymerization is conducted at 130 °C for 2.5 h. After evaporation of volatile components 5.1 g (21%) polymer are obtained.

GPC : $M_n = 1200$, $M_w = 1700$, $PD = 1.4$

Example B20. In situ preparation of Initiator from compound 104 and V-65 with simultaneous polymerization of n-butylacrylate

0.670 g (4.7 mmol) of compound 104, 1.162 g (4.7 mmol) of compound V-65, 30 g (234 mmol) n-butylacrylate and 15 g octane are mixed in a 100 ml flask and degassed. The mixture is stirred for 30 min. at 80 °C. The temperature is slowly raised to 130 °C. The mixture is polymerized at 130 °C for 2.5 h. After evaporation of volatile components 11.4 g polymer are obtained, corresponding to 38% conversion.

GPC : $M_n = 2800$, $M_w = 5700$, $PD = 2.0$

Example B21. In situ preparation of initiator from compound 104 and V-65 with subsequent polymerization of n-butylacrylate

0.670g (4.7 mmol) of compound 104, 2.034 g (8.2 mmol) of compound V-65 and 15 g octane are mixed in a 100 ml flask and degased. The mixture is stirred for 1.25 h at 80°C.

30 g (234 mmol) of n-butylacrylate are added and the temperature is slowly raised to 130°C. The mixture is polymerized at this temperature for 3 h. After evaporation of volatile components 80% conversion are obtained.

GPC : Mn = 6200, Mw = 12200, PD = 1.97

Example B22. Polymerization of n-butylacrylate using compound 105

In a 50 ml three neck flask, equipped with thermometer, cooler and magnetic stirrer, 1643 mg (6,24 mmol) of compound 101 and 20 g (156 mmol) of n-butylacrylate are mixed and degased. The clear solution obtained is heated under argon to 115 °C. Polymerization starts spontaneously and the temperature rises to 130° C. After 15 minutes, the exothermal reaction slowly stops and the viscosity of the solution increases. The reaction mixture is stirred for an additional 15 minutes at 145 °C and is then cooled to 80 °C. The remaining monomer is removed by evaporation under high vacuum. 19,3 g (97%) of the initial monomer have reacted. A clear colourless viscous fluid is obtained.

MALDI-MS: Mn = 3000, Mw = 5300, PD = 1,7

GPC: Mn = 3100, Mw = 5400, PD = 1,7

Example B23. Polymerization of n-butylacrylate using compound 106

In a 50 ml three neck flask, equipped with thermometer, cooler and magnetic stirrer, 804 mg (2,34 mmol) of compound 102 and 20 g (156 mmol) of n-butylacrylate are mixed and degased. The clear solution obtained is heated under argon to 145 °C. Polymerization starts spontaneously and the temperature rises to 170° C. After 15 minutes, the exothermal reaction slowly stops and the viscosity of the solution increases. The reaction mixture is stirred for an additional 15 minutes at 145 °C and is then cooled to 80 °C. The remaining monomer is removed by evaporation under high vacuum. 19,5 g (98%) of the initial monomer have reacted. A clear colourless viscous fluid is obtained.

MALDI-MS: Mn = 4600, Mw = 7300, PD = 1,6

Example B24. Polymerization of n-butylacrylate using compound 106

1608 mg (4.68 mmol) of compound 106 and 20 g (156 mmol) n-butylacrylate in 10 ml n-octane are reacted at 130 °C for 2.5 h. After evaporation of volatile components 17.1 g (79%) polymer are obtained.

GPC : Mn=3400, Mw = 5700, PD = 1.7

Example B25. Polymerization of acrylic acid-2-ethoxyethylester using compound 105

1.96 g (4.16mmol) of compound 105, 20 g (139 mmol) acrylic acid-2-ethoxyethylester in 10 g toluene are polymerized in a 50 ml flask at 115 °C for 5 h. After evaporation of volatile components 17.4 g (87%) of a viscous polymer are obtained.

GPC : Mn = 3900, Mw = 7600, PD = 1.9

Example B26. Polymerization of methacrylic acid-2-dimethylaminoethylester using compound 106

1.309 g (3.81 mmol) of compound 106, 20 g (127 mmol) methacrylic acid-2-dimethylaminoethylester and 10 g octane are reacted at 130 °C for 2.5 h. After evaporation of volatile components 18.4 g (92%) of a viscous to solid polymer is obtained.

GPC : Mn = 4100, Mw = 8300, PD = 2

Example B27. Blockcopolymerization of n-butylacrylate and methacrylic acid-2-dimethylamino-ethylester using compound 106

2.411 g (7.02 mmol) of compound 106 and 20 g (156 mmol) n-butylacrylate, dissolved in 10 g n-octane, are reacted at 130 °C for 2.5 h. Volatile components are evaporated under vacuum at 80° C and the residue is isolated. Conversion is 93%.

In a second step 12.3 g (78 mmol) methacrylic acid-2-dimethylaminoethylester and 16 g n-octane are added and at 130 °C for 2.5 h polymerized. After evaporation of volatile components 29.8 g (92%) copolymer are obtained.

GPC : Mn = 4200, Mw = 8600, PD = 2

Example B28. Blockcopolymerization of n-butylacrylate and iso-butylacrylate using compound 105

1.233 g (4.68 mmol) of compound 105 and 20 g (156 mmol) n-butylacrylate are reacted at 130 °C for 40 min. The reaction mixture is cooled down to 100 °C and 20 g (156 mmol) iso-

butylacrylate are added. Reaction is continued at 130 °C for 1.5 h. After evaporation of volatile components 34.7 g (87%) copolymer are obtained.

GPC : Mn = 6200, Mw = 11600, PD = 1.8

Example B29. Random copolymer of n-butylacrylate and methacrylic acid-2-dimethylaminoethylester using compound 106

2.617 g (7.62 mmol) of compound 106, 16.3 g (127 mmol) n-butylacrylate, 20 g (127 mmol) methacrylic acid-2-dimethylaminoethylester and 18 g octane are reacted at 130 °C for 2.5 h. After evaporation of volatile components 36.4 g (93%) of a viscous liquid are obtained.

GPC : Mn = 3800, Mw = 5800, PD = 1.5

Example B30. Block-copolymer of n-butylacrylate and methacrylic acid-2-dimethylaminoethylester (MADMAEE) using compound 106

2,617 g (7.62 mmol) of compound 106 in 8.2 g octane and 16.3 g (127 mmol) n-butylacrylate are polymerized at 130 °C for 2.5 h. After evaporation of volatile components 17.8 g (93%) of the first polymer block are obtained. 18 g octane and 20 g (127 mmol) MADMAEE are subsequently polymerized at 130 °C for 2.5 h. After evaporation of volatile components 36.3 g (93 %) of the block-copolymer are obtained.

GPC: Mn = 3300, Mw = 11300, PD = 3.4

Example B31. Random copolymer of n-butylacrylate and acrylic acid using compound 105

1.3 g (4.93 mmol) of compound 105, 18.9 g (147.8 mmol) n-butylacrylate, 1.18 g (16.4 mmol) acrylic acid in 10 g octane are reacted at 130 °C for 2.5 h. After evaporation of volatile components 20.7 g (97%) of a clear viscous liquid are obtained.

GPC : Mn = 3800, Mw = 8200, PD = 2.2

Example B32. Triblock-copolymer of n-butylacrylate / methacrylic acid-2-dimethylaminoethylester / n-butylacrylate using compound 106

3.617 g (10.53 mmol) of compound 106, 7.5 g (58.5 mmol) n-butylacrylate, 9.2 g (58.5 mmol) MADMAEE and again 7.5 g (58.5 mmol) n-butylacrylate in octane are polymerized successively according to example B30 at a temperature of 130 °C for 2.5 h for each step. Conversions for each step are 91 %, 95 % and 34 % .

GPC : $M_n = 2800$, $M_w = 4400$, $PD = 1.7$

Example 33. Homopolymerization of styrene

0.679 g (2mmol) of compound 106, 20.9 g (200 mmol) styrene and 20 g toluene are refluxed for 6 h. After evaporation of volatile components 19.6 g (94%) polymer are obtained.

GPC : $M_n = 9000$, $M_w = 10800$, $PD = 1.2$

Example B34. Homopolymerization of styrene

0.527 g (2 mmol) of compound 105, 20.9 g (200 mmol) styrene and 20 g toluene are refluxed for 6 h. After evaporation of volatile components 19.6 g (94%) polymer are obtained.

GPC : $M_n = 9400$, $M_w = 11400$, $PD = 1.2$

Example B35. Pseudo-block-copolymerisation of polystyrene of example B34 with styrene

5 g of the polymer of example 34 are mixed with 5 g styrene and 20 g toluene. The solution is degased and reacted at 110 °C for 6 h. After evaporation of volatile components 7.7 g (54%) polymer are obtained.

GPC : $M_n = 13500$, $M_w = 17500$, $PD = 1.3$

Example B36. Block-copolymer of styrene and n-butylacrylate

62.5 g (0.6 mol) styrene are polymerized with 1.68 g (6 mmol) of compound 105 in 40 g octane at 110 °C for 6 h. 42 g (66%) of polystyrene are obtained.

GPC : $M_n = 9400$, $M_w = 11400$, $PD = 1.2$

To 30 g of the polystyrene 40 g (312 mmol) n-butylacrylate and 40 g octan are added. The mixture is heated to 130 °C for 6 h under stirring. n-butylacrylate is reacted to 98% and 69 g of the block copolymer are obtained.

GPC : $M_n = 13500$, $M_w = 19100$, $PD = 1.4$

Example B37. In situ preparation of initiator from compound 107 and azobisisobutyronitrile with simultaneous polymerization of n-butylacrylate

In a 100 ml flask 0.397 g (3.12 mmol) of compound 107, 0.512 g (3.12 mmol) AIBN, 20 g (156 mmol) n-butylacrylate and 10 g octane are mixed. The mixture is stirred at 80°C for 2 h. The temperature is slowly raised to 130 °C and the mixture is reacted for 2.5 h at this temperature. After evaporation of volatile components 17.5 g (83 %) of a viscous liquid are obtained.

GPC : $M_n = 6500$, $M_w = 13200$, $PD = 2$

Example B38. In situ preparation of initiator from compound 107 and V-65 with simultaneous polymerization of n-butylacrylate

In a 100 ml flask 0.397 g (3.12 mmol) of compound 107, 0.775 g (3.12 mmol) of compound V-65, 20 g (156 mmol) n-butylacrylate and 10 g octane are mixed. The mixture is stirred for 30 min. at 80° C. Temperature is raised slowly to 130° C and the mixture is reacted for 2.5 h. After evaporation of volatile components 65% conversion is obtained.

GPC : $M_n = 5400$, $M_w = 9200$, $PD = 1.7$

Example B39. In situ preparation of initiator from compound 107 and V-65 with subsequent polymerization of n-butylacrylate

In a 100 ml flask 0.595 g (4.7 mmol) of compound 107, 2.034 g (8.2 mmol) of compound V-65 and 15 g octane are mixed. The mixture is stirred at 80° C for 1.25 h. 30 g (234 mmol) n-butylacrylate are added and the temperature is slowly raised to 130°C. The mixture is allowed to react for 5 h at this temperature. After evaporation of volatile components 20% conversion is achieved.

GPC : $M_n = 5800$, $M_w = 9000$, $PD = 1.66$

Example B40. In situ preparation of initiator from compound 107 and V-70 with simultaneous polymerization of n-butylacrylate

In a 100 ml flask 0.595 g (4.7 mmol) of compound 107, 2.526 g (8.2 mmol) of compound V-70, 30 g (234 mmol) n-butylacrylate and 15 g octane are mixed. The mixture is stirred for 15 min. at 60° C. Temperature is raised slowly to 130° C and the mixture is reacted for 5 h. After evaporation of volatile components 66% conversion is obtained.

GPC : $M_n = 4400$, $M_w = 7600$, $PD = 1.73$

Example B41. In situ preparation of initiator from compound 107 and V-70 with subsequent polymerization of n-butylacrylate

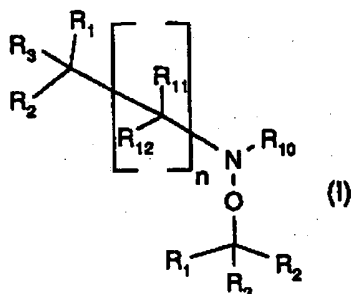
In a 100 ml flask 0.595 g (4.7 mmol) of compound 107, 2.526 g (8.2 mmol) of compound V-70 and 15 g octane are mixed. The mixture is stirred at 60° C for 1.25 h. 30 g (234 mmol) n-butylacrylate are added and the temperature is slowly raised to 130°C. The mixture is allowed to react for 5 h at this temperature. After evaporation of volatile components 20% conversion is achieved.

GPC : Mn = 5500, Mw = 9400, PD = 1.72

What is claimed is

1. A polymerizable composition, comprising

- a) at least one ethylenically unsaturated monomer or oligomer, and
b) an initiator compound of formula (I)



wherein n is 0 or 1

R_1 , R_2 , R_3 are each independently of one another hydrogen, halogen, NO_2 , cyano, $-\text{CONR}_5\text{R}_6$, $-(\text{R}_9)\text{COOR}_4$, $-\text{C}(\text{O})-\text{R}_7$, $-\text{OR}_8$, $-\text{SR}_8$, $-\text{NHR}_8$, $-\text{N}(\text{R}_8)_2$, carbamoyl, $\text{di}(\text{C}_1\text{-C}_{18}\text{alkyl})\text{carbamoyl}$, $-\text{C}(=\text{NR}_5)(\text{NHR}_6)$;

unsubstituted $\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_2\text{-C}_{18}\text{alkenyl}$, $\text{C}_2\text{-C}_{18}\text{alkynyl}$, $\text{C}_7\text{-C}_9\text{phenylalkyl}$, $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom; or

$\text{C}_1\text{-C}_{18}\text{alkyl}$, $\text{C}_2\text{-C}_{18}\text{alkenyl}$, $\text{C}_2\text{-C}_{18}\text{alkynyl}$, $\text{C}_7\text{-C}_9\text{phenylalkyl}$, $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ or $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, $\text{C}_1\text{-C}_4\text{alkoxy}$, $\text{C}_1\text{-C}_4\text{alkylthio}$, $\text{C}_1\text{-C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$; or

phenyl, naphthyl, which are unsubstituted or substituted by $\text{C}_1\text{-C}_4\text{alkyl}$, $\text{C}_1\text{-C}_4\text{alkoxy}$, $\text{C}_1\text{-C}_4\text{alkylthio}$, halogen, cyano, hydroxy, carboxy, $\text{C}_1\text{-C}_4\text{alkylamino}$ or $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})\text{amino}$; or R_2 and R_3 , together with the linking carbon atom, form a $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ radical, a $(\text{C}_4\text{-C}_{12}\text{cycloalkanon})\text{-yl}$ radical or a $\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ radical containing at least one O atom and/or a NR_8 group; or if n is 1



R_4 is hydrogen, $\text{C}_1\text{-C}_{18}\text{alkyl}$, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R_5 and R_6 are hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is substituted by at least one hydroxy group or, taken together, form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} -alkylene bridge interrupted by at least one O or/and NR_8 atom;

R_7 is hydrogen, C_1 - C_{18} alkyl or phenyl;

R_8 is hydrogen, C_1 - C_{18} alkyl or C_2 - C_{18} alkyl which is substituted by at least one hydroxy group;

R_9 is C_1 - C_{12} alkylene or a direct bond;

R_{10} is C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, C_7 - C_{11} phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, C_7 - C_{11} phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino;

if n is 1

R_{11} is C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R_{10} and R_{11} together form a C_2 - C_{12} alkylene bridge, a C_3 - C_{12} alkylene-on bridge or a C_2 - C_{12} alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C_1 - C_{18} alkyl, hydroxy(C_1 - C_4)alkyl, phenyl, C_7 - C_9 phenylalkyl, NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino,

R_{12} is hydrogen, $-(R_9)COOR_9$, cyano, $-OR_9$, $-SR_9$, $-NHR_9$, $-N(R_9)_2$, $-NH-C(O)-R_9$, unsubstituted C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino; or R₁₁ and R₁₂ together with the linking carbon atom form a C₃-C₁₂cycloalkyl radical; with the proviso that bis-(2-cyano-2-propyl)-N-phenylhydroxylamine is excluded and if n = 0 R₁₀ is different from the group -CR₁R₂R₃.

2. A composition according to claim 1, which additionally comprises a solvent selected from the group consisting of water, alcohols, esters, ethers, ketones, amides, sulfoxides, hydrocarbons and halogenated hydrocarbons.

3. A composition according to claim 1, wherein the ethylenically unsaturated monomer or oligomer is selected from the group consisting of styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters or (alkyl)acrylamides.

4. A composition according to claim 3 wherein the ethylenically unsaturated monomer is styrene, a-methyl styrene, p-methyl styrene or a compound of formula CH₂=C(R_a)-(C=Z)-R_b, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH₂, O(Me), glycidyl, unsubstituted C₁-C₁₈alkoxy or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino; Me is a monovalent metal atom; Z is oxygen or sulfur.

5. A composition according to claim 4, wherein R_a is hydrogen or methyl, R_b is NH₂, glycidyl, unsubstituted or with hydroxy substituted C₁-C₄alkoxy, unsubstituted C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, hydroxy-substituted C₁-C₄alkylamino or hydroxy-substituted di(C₁-C₄alkyl)amino; and Z is oxygen.

6. A polymerizable composition according to claim 5, wherein the ethylenically unsaturated monomer is methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, glycidylacrylates, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, glycidyl(meth)acrylates, acrylonitrile, acrylamide or methacrylamide.

7. A composition according to claim 1, wherein

n is 0 or 1;

R₁, R₂, R₃ are each independently of one another NO₂, cyano, -(R₉)COOR₄, -CONR₅R₆, -C(O)-R₇, -OR₈, carbamoyl, di(C₁-C₁₈alkyl)carbamoyl, -C(=NR₅)(NHR₆);

unsubstituted C₁-C₁₈alkyl, C₇-C₉phenylalkyl or C₃-C₁₂cycloalkyl; or

C₁-C₁₈alkyl, C₇-C₉phenylalkyl or C₃-C₁₂cycloalkyl, which are substituted by amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;

or R₂ and R₃, together with the linking carbon atom, form a C₃-C₁₂ cycloalkyl radical;

R₄ is, C₁-C₁₈alkyl, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R₅ and R₆ are hydrogen, C₁-C₁₈alkyl, C₂-C₁₈alkyl which is substituted by at least one hydroxy group or, taken together, form a C₂-C₁₂alkylene bridge;

R₇ is hydrogen, C₁-C₁₈alkyl or phenyl;

R₈ is C₁-C₁₈alkyl or C₂-C₁₈alkyl which is substituted by at least one hydroxy group; and

R₉ is C₁-C₄alkyl or a direct bond.

R₁₀ is C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, phenyl, C₈-C₁₁phenylalkyl or C₃-C₁₂cycloalkyl;

if n is 1

R₁₁ is C₁-C₁₈alkyl, C₇-C₉phenylalkyl or C₃-C₁₂cycloalkyl or

R₁₀ and R₁₁ together form a C₂-C₁₂alkylene bridge or a C₂-C₁₂alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C₁-C₁₈alkyl;

R₁₂ is, unsubstituted C₁-C₁₈alkyl, phenyl, C₇-C₉phenylalkyl or C₃-C₁₂cycloalkyl or

R₁₁ and R₁₂ together with the linking carbon atom, form a C₃-C₁₂ cycloalkyl radical.

8. A composition according to claim 7, wherein

n is 0 or 1;

R₁, R₂, R₃ are each independently of one another NO₂, cyano, -(R₉)COOR₄, -CONR₅R₆, -C(O)-R₇, -OR₈, carbamoyl, di(C₁-C₈alkyl)carbamoyl, -C(=NR₅)(NHR₆);

unsubstituted C₁-C₁₂alkyl, C₇-C₉phenylalkyl or C₅-C₇cycloalkyl; or

C₁-C₈alkyl, C₇-C₉phenylalkyl or C₅-C₇cycloalkyl or, which are substituted by amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;

or phenyl,

or R₂ and R₃, together with the linking carbon atom, form a C₅-C₇ cycloalkyl radical;

R₄ is C₁-C₈alkyl, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R_5 and R_6 are hydrogen, C_1 - C_8 alkyl, C_2 - C_8 alkyl which is substituted by at least one hydroxy group or, taken together, form a C_2 - C_8 alkylene bridge;

R_7 is hydrogen, C_1 - C_8 alkyl or phenyl;

R_8 is C_1 - C_8 alkyl or C_2 - C_8 alkyl which is substituted by at least one hydroxy group;

R_9 is C_1 - C_4 alkylene or a direct bond;

R_{10} is C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom or phenyl;

If n is 1

R_{11} is C_1 - C_{18} alkyl, phenyl or C_7 - C_8 phenylalkyl or

R_{10} and R_{11} together form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C_1 - C_{18} alkyl;

R_{12} is unsubstituted C_1 - C_{18} alkyl or phenyl.

9. A composition according to claim 8, wherein

n is 0 or 1;

R_1 , R_2 , R_3 are each independently of one another NO_2 , cyano, $-C(O)-R_7$, $-OR_8$, unsubstituted C_1 - C_{12} alkyl or phenyl, which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino;

or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;

R_7 is, C_1 - C_8 alkyl or phenyl;

R_8 is C_1 - C_8 alkyl or C_2 - C_8 alkyl which is substituted by at least one hydroxy group and

R_{10} is C_4 - C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, phenyl or C_6 - C_{11} phenylalkyl;

If n is 1

R_{11} is C_1 - C_{12} alkyl; or

R_{10} and R_{11} together form a C_2 - C_8 alkylene bridge which is unsubstituted or substituted with C_1 - C_4 alkyl;

R_{12} is hydrogen, unsubstituted C_1 - C_4 alkyl or phenyl.

10. A composition according to claim 1, wherein

n is 0

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1 - C_{12} alkyl or phenyl;

or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;

R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_6 - C_{11} phenylalkyl or phenyl.

11. A composition according to claim 1, wherein

n is 1

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1 - C_{12} alkyl or phenyl;
or R_2 and R_3 , together with the linking carbon atom, form a C_5 - C_7 cycloalkyl radical;

R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_6 - C_{11} phenylalkyl or phenyl; or

R_{10} and R_{11} together form a C_2 - C_6 alkylene bridge which is unsubstituted or substituted with C_1 - C_4 alkyl; and

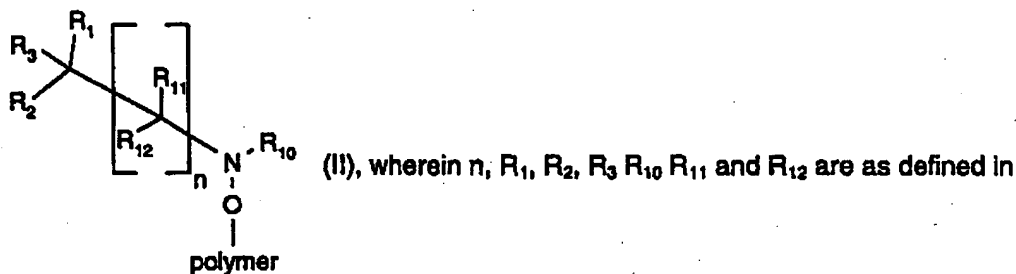
R_{12} is C_1 - C_4 alkyl.

12. A process for preparing an oligomer, a cooligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises (co)polymerizing the monomer or monomers/oligomers in the presence of an initiator compound of formula (I) according to claim 1 under reaction conditions capable of effecting scission of the O-C bond to form two free radicals, the radical $\bullet CR_1R_2R_3$ being capable of initiating polymerization.

13. A process according to claim 12, wherein the scission of the O-C bond is effected by ultrasonic treatment, heating or exposure to actinic radiation.

14. A process according to claim 12, wherein the scission of the O-C bond is effected by heating and takes place at a temperature of between 50°C and 160°C .

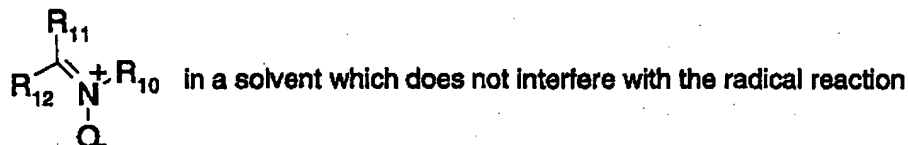
15. A process according to claim 12 for preparing a block copolymer involving at least two stages, which comprises forming a polymer with alkoxyamine end groups of the general structure of formula II



claim 1, the polymer containing the initiator group $\bullet CR_1R_2R_3$ and having the oxyamine group

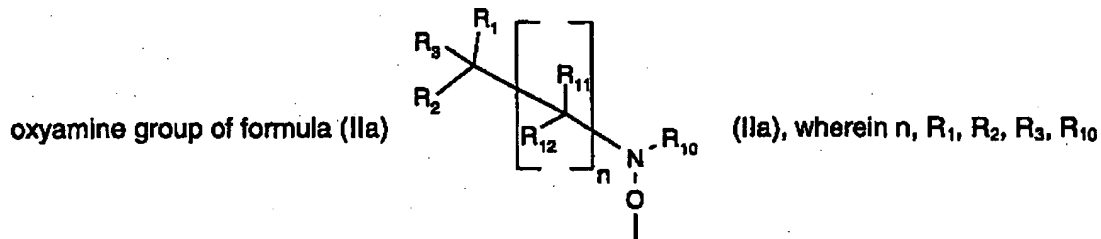
essentially attached as terminal group, and adding a further monomer followed by heating to form a block copolymer.

16. A process for preparing a oligomer, a cooligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises
generating a free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) from a compound capable of eliminating a neutral molecule, or undergoing C-C bond-scission upon thermal or photochemical treatment, or by hydrogen abstraction from a compound $\text{R}_1\text{R}_2\text{R}_3\text{C-H}$ in reaction with reactive radicals, and reacting the free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) with a compound of formula R_{10}NO or



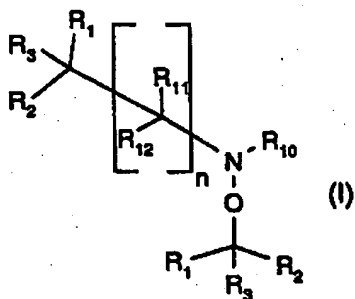
in the presence of at least one ethylenically unsaturated monomer or oligomer.

17. A polymer or oligomer, having at least one Initiator group $-\text{CR}_1\text{R}_2\text{R}_3$ and at least one



R_{11} and R_{12} are as defined in claim 1, obtainable by the process according to claim 12.

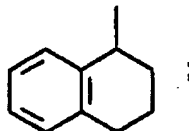
18. A compound of formula (I)



wherein n is 0 or 1

R_1, R_2, R_3 are each independently of one another hydrogen, halogen, NO_2 , cyano, $-CONR_5R_6$, $-(R_9)COOR_4$, $-C(O)-R_7$, $-OR_8$, $-SR_8$, $-NHR_8$, $-N(R_8)_2$, carbamoyl, $di(C_1-C_{18}alkyl)carbamoyl$, $-C(=NR_5)(NHR_6)$; unsubstituted $C_1-C_{18}alkyl$, $C_2-C_{18}alkenyl$, $C_2-C_{18}alkynyl$, $C_7-C_9phenylalkyl$, $C_3-C_{12}cycloalkyl$ or $C_3-C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom; or $C_1-C_{18}alkyl$, $C_2-C_{18}alkenyl$, $C_2-C_{18}alkynyl$, $C_7-C_9phenylalkyl$, $C_3-C_{12}cycloalkyl$ or $C_3-C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, $C_1-C_4alkoxy$, $C_1-C_4alkylthio$, $C_1-C_4alkylamino$ or $di(C_1-C_4alkyl)amino$; or phenyl, naphthyl, which are unsubstituted or substituted by C_1-C_4alkyl , $C_1-C_4alkoxy$, $C_1-C_4alkylthio$, halogen, cyano, hydroxy, carboxy, $C_1-C_4alkylamino$ or $di(C_1-C_4alkyl)amino$; or R_2 and R_3 , together with the linking carbon atom, form a $C_3-C_{12}cycloalkyl$ radical, a $(C_4-C_{12}cycloalkanon)-yl$ radical or a $C_3-C_{12}cycloalkyl$ radical containing at least one O atom

and/or a NR_8 group; or if n is 1 R_2  are a group



R_4 is hydrogen, $C_1-C_{18}alkyl$, phenyl, an alkali metal cation or a tetraalkylammonium cation; R_5 and R_6 are hydrogen, $C_1-C_{18}alkyl$, $C_2-C_{18}alkyl$ which is substituted by at least one hydroxy group or, taken together, form a $C_2-C_{12}alkylene$ bridge or a $C_2-C_{12}alkylene$ bridge interrupted by at least one O or/and NR_8 atom; R_7 is hydrogen, $C_1-C_{18}alkyl$ or phenyl; R_8 is hydrogen, $C_1-C_{18}alkyl$ or $C_2-C_{18}alkyl$ which is substituted by at least one hydroxy group; R_9 is $C_1-C_{12}alkylene$ or a direct bond; R_{10} is $C_4-C_{18}alkyl$ bound via a tertiary C-atom to the nitrogen atom, $C_8-C_{11}phenylalkyl$, $C_3-C_{12}cycloalkyl$ or $C_3-C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom; or $C_4-C_{18}alkyl$ bound via a tertiary C-atom to the nitrogen atom, $C_8-C_{11}phenylalkyl$, $C_3-C_{12}cycloalkyl$ or $C_3-C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, $C_1-C_4alkoxy$, $C_1-C_4alkylthio$, $C_1-C_4alkylamino$ or $di(C_1-C_4alkyl)amino$; or phenyl, naphthyl, which are unsubstituted or substituted by C_1-C_4alkyl , $C_1-C_4alkoxy$, $C_1-C_4alkylthio$, halogen, cyano, hydroxy, carboxy, $C_1-C_4alkylamino$ or $di(C_1-C_4alkyl)amino$; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; if n is 1

R_{11} is C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R_{10} and R_{11} together form a C_2 - C_{12} alkylene bridge, a C_3 - C_{12} alkylen-on bridge or a C_2 - C_{12} alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C_1 - C_{18} alkyl, hydroxy(C_1 - C_4)alkyl, phenyl, C_7 - C_9 phenylalkyl, NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino, or

R_{12} is hydrogen, $-(R_9)COOR_4$, cyano, $-OR_8$, $-SR_8$, $-NHR_8$, $-N(R_8)_2$, $-NH-C(O)-R_8$, unsubstituted C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom; or

C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl, C_7 - C_9 phenylalkyl, C_3 - C_{12} cycloalkyl or C_3 - C_{12} cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, C_1 - C_4 alkylamino or $di(C_1$ - C_4 alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, cyano, hydroxy, carboxy, C_1 - C_4 alkylamino, $di(C_1$ - C_4 alkyl)amino; or

R_{11} and R_{12} together with the linking carbon atom, form a C_3 - C_{12} cycloalkyl radical;

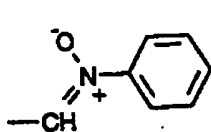
with the proviso that

if n is 0 R_{10} is different from the group $-CR_1R_2R_3$, and if R_1 is CN and R_2 and R_3 are methyl, R_{10} is not phenyl, phenyl substituted by methyl, 2,4,6-trimethyl, chlor, fluor, (3-methyl,4-fluor), (3-fluor, 4-methyl), (4-fluor, 2-methyl), (4-fluor, 2-methoxy), (2-fluor, 3,5-methyl), 2,5-di-tert.butyl, nitro, 3,5-dinitro or 2 $(-O-C(CH_3)_2CN)$ 4-nitro; and

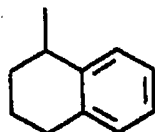
if n is 1, R_{12} is hydrogen, R_{10} phenyl or benzyl and R_{11} phenyl,

R_1 , R_2 and R_3 are not a group $-C(CH_3)_2CN$, $-C(CH_3)_2COOCH_3$, benzyl, methylbenzyl,

dimethylbenzyl,



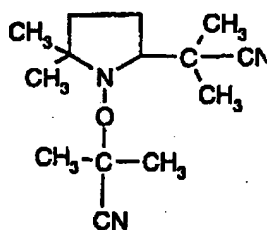
or



and

- 53 -

the compound according to formula I is not



19. A compound according to claim 18, wherein

n is 0 or 1;

R_1 , R_2 , R_3 are each independently of one another NO_2 , cyano, $-\text{C}(\text{O})-\text{R}_7$, $-\text{OR}_8$, unsubstituted C_1-C_{12} alkyl or phenyl, which is unsubstituted or substituted by C_1-C_4 alkyl, C_1-C_4 alkoxy, cyano, hydroxy, carboxy, C_1-C_4 alkylamino or $\text{di}(\text{C}_1-\text{C}_4\text{alkyl})\text{amino}$;

or R_2 and R_3 , together with the linking carbon atom, form a C_5-C_7 cycloalkyl radical;

R_7 is, C_1-C_8 alkyl or phenyl;

R_8 is C_1-C_8 alkyl or C_2-C_8 alkyl which is substituted by at least one hydroxy group and

R_{10} is C_4-C_{18} alkyl bound via a tertiary C-atom to the nitrogen atom, phenyl or C_8-C_{11} phenylalkyl;

If n is 1

R_{11} is C_1-C_{18} alkyl, C_7-C_9 phenylalkyl or C_3-C_{12} cycloalkyl or

R_{10} and R_{11} , together form a C_2-C_6 alkylene bridge which is unsubstituted or substituted with C_1-C_4 alkyl;

R_{12} is , unsubstituted C_1-C_4 alkyl or phenyl.

20. A compound according to claim 18, wherein

n is 0

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1-C_{12} alkyl or phenyl;

or R_2 and R_3 , together with the linking carbon atom, form a C_5-C_7 cycloalkyl radical;

R_{10} is C_4-C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_8-C_{11} phenylalkyl or phenyl.

21. A compound according to claim 18, wherein

n is 1

R_1 is cyano;

R_2 and R_3 are each independently of one another unsubstituted C_1-C_{12} alkyl or phenyl;

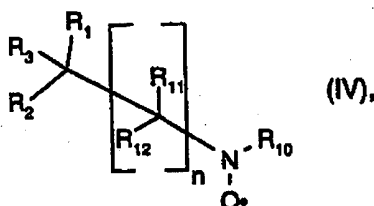
or R_2 and R_3 , together with the linking carbon atom, form a C_5-C_7 cycloalkyl radical;

R_{10} is C_4 - C_{12} alkyl bound via a tertiary C-atom to the nitrogen atom, C_9 - C_{11} phenylalkyl or phenyl; or

R_{10} and R_{11} together form a C_2 - C_6 alkylene bridge which is unsubstituted or substituted with C_1 - C_4 alkyl; and

R_{12} is C_1 - C_4 alkyl.

22. A compound of formula (IV)



wherein n is 0 or 1

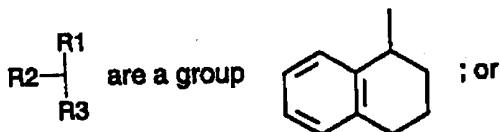
R_1 , R_2 , R_3 are each independently of one another hydrogen, halogen, NO_2 , cyano, $-CONR_5R_6$, $-(R_6)COOR_4$, $-C(O)-R_7$, $-OR_8$, $-SR_8$, $-NHR_8$, $-N(R_8)_2$, carbamoyl, $di(C_1-C_{18}alkyl)carbamoyl$, $-C(=NR_5)(NHR_6)$;

unsubstituted C_1 - $C_{18}alkyl$, C_2 - $C_{18}alkenyl$, C_2 - $C_{18}alkynyl$, C_7 - $C_9phenylalkyl$, C_3 - $C_{12}cycloalkyl$ or C_3 - $C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom; or

C_1 - $C_{18}alkyl$, C_2 - $C_{18}alkenyl$, C_2 - $C_{18}alkynyl$, C_7 - $C_9phenylalkyl$, C_3 - $C_{12}cycloalkyl$ or C_3 - $C_{12}cycloalkyl$ containing at least one nitrogen or oxygen atom, which are substituted by NO_2 , halogen, amino, hydroxy, cyano, carboxy, C_1 - $C_4alkoxy$, C_1 - $C_4alkylthio$, C_1 - $C_4alkylamino$ or $di(C_1-C_4alkyl)amino$; or

phenyl, naphthyl, which are unsubstituted or substituted by C_1 - C_4alkyl , C_1 - $C_4alkoxy$, C_1 - $C_4alkylthio$, halogen, cyano, hydroxy, carboxy, C_1 - $C_4alkylamino$ or $di(C_1-C_4alkyl)amino$;

or R_2 and R_3 , together with the linking carbon atom, form a C_3 - $C_{12}cycloalkyl$ radical, a $(C_4-C_{12}cycloalkanon)-yl$ radical or a C_3 - $C_{12}cycloalkyl$ radical containing at least one O atom and/or a NR_8 group; or if n is 1



R_4 is hydrogen, C_1 - $C_{18}alkyl$, phenyl, an alkali metal cation or a tetraalkylammonium cation;

R_5 and R_6 are hydrogen, C_1 - $C_{18}alkyl$, C_2 - $C_{18}alkyl$ which is substituted by at least one hydroxy group or, taken together, form a C_2 - $C_{12}alkylene$ bridge or a C_2 - $C_{12}alkylene$ bridge interrupted by at least one O or/and NR_8 atom;

R₇ is hydrogen, C₁-C₁₈alkyl or phenyl;

R₈ is hydrogen, C₁-C₁₈alkyl or C₂-C₁₈alkyl which is substituted by at least one hydroxy group;

R₉ is C₁-C₁₂alkylene or a direct bond;

R₁₀ is C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, C₀-C₁₁phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or C₄-C₁₈alkyl bound via a tertiary C-atom to the nitrogen atom, C₉-C₁₁phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom;

If n is 1

R₁₁ is C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or

C₁-C₁₈alkyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or a polycyclic cycloaliphatic ring system or a polycyclic cycloaliphatic ring system with at least one di- or trivalent nitrogen atom; or

R₁₀ and R₁₁ together form a C₂-C₁₂alkylene bridge, a C₃-C₁₂alkylene-on bridge or a C₂-C₁₂alkylene bridge which is interrupted by at least one O or N atom, which bridges are unsubstituted or substituted with C₁-C₁₈alkyl, hydroxy(C₁-C₄)alkyl, phenyl, C₇-C₉phenylalkyl, NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino;

R₁₂ is hydrogen, -(R₉)COOR₄, cyano, -OR₈, -SR₈, -NHR₈, -N(R₈)₂, -NH-C(O)-R₈, unsubstituted C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom; or C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkynyl, C₇-C₉phenylalkyl, C₃-C₁₂cycloalkyl or C₃-C₁₂cycloalkyl containing at least one nitrogen or oxygen atom, which are substituted by NO₂, halogen, amino, hydroxy, cyano, carboxy, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkylamino or di(C₁-C₄alkyl)amino; or

phenyl, naphthyl, which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, halogen, cyano, hydroxy, carboxy, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino; or

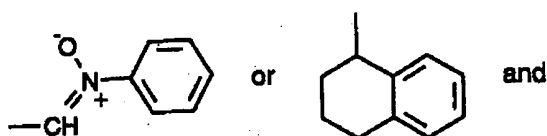
R₁₁ and R₁₂ together with the linking carbon atom, form a C₃-C₁₂ cycloalkyl radical; with the proviso that

if n is 0 R₁₀ is different from the group -CR₁R₂R₃, and if R₁ is CN and R₂ and R₃ are methyl, R₁₀ is not phenyl, phenyl substituted by methyl, 2,4,6-trimethyl, chlor, fluor, (3-methyl,4-fluor), (3-fluor, 4-methyl), (4-fluor, 2-methyl), (4-fluor, 2-methoxy), (2-fluor, 3,5-methyl), 2,5-di-tert.butyl, nitro, 3,5-dinitro or 2 (-O-C(CH₃)₂CN) 4-nitro; and

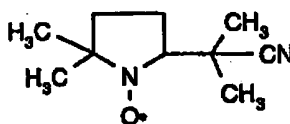
if n is 1, R₁₂ is hydrogen, R₁₀ phenyl or benzyl and R₁₁ phenyl,

R₁, R₂ and R₃ are not a group -C(CH₃)₂CN, -C(CH₃)₂COOCH₃, benzyl, methylbenzyl,

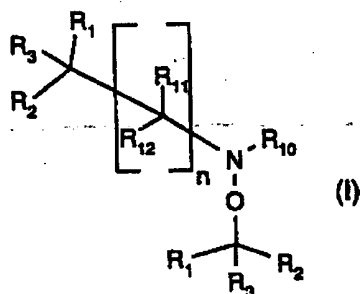
dimethylbenzyl,



the compound according to formula IV is not

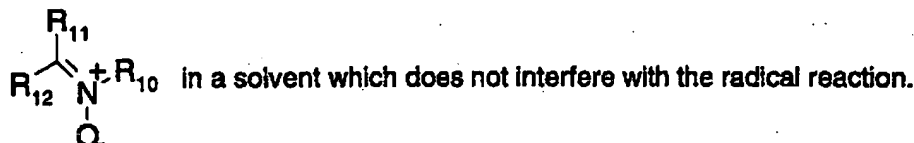


23. A process for preparing a compound of formula (I) according to claim 1

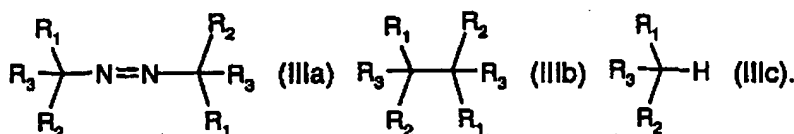


by generating a free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) from a compound capable of eliminating a neutral molecule, or undergoing C-C bond-scission upon thermal or photochemical treatment, or by hydrogen abstraction from a compound $\text{R}_1\text{R}_2\text{R}_3\text{C-H}$ in reaction with reactive radicals, and

reacting the free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ (V) with a compound of formula R_{10}NO or



24. A process according to claim 23 wherein the free radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ is prepared by heating or irradiation of a compound of formula IIIa, IIIb or IIIc



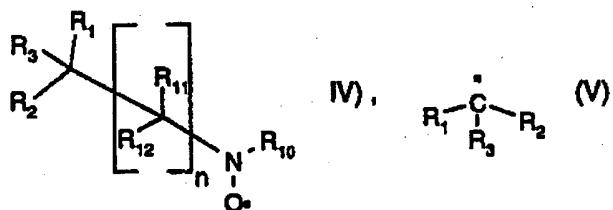
25. A process according to claim 23, wherein the radical $\bullet\text{CR}_1\text{R}_2\text{R}_3$ is prepared by heating at a temperature from 40 to 150° C.

26. A process according to claim 23, wherein the free radical source is 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(1-cyclohexanecarbonitrile), 4,4'-azobis(4-cyanopentanoic acid), 2,2'-azobis(isobutyramide), dihydrate, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, dimethyl-2,2'-azobisisobutyrate, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), 2,2'-azobis(N,N'-dimethyleneisobutyramidine), free base or hydrochloride, 2,2'-azobis(2-amidinopropane), free base or hydrochloride, 2,2'-azobis[2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide] or 2,2'-azobis[2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide.

27. Use of a compound of formula I according to claim 1 for polymerizing ethylenically unsaturated monomers.

28. A polymerizable composition, comprising

- a) at least one ethylenically unsaturated monomer or oligomer,
- b) a compound of formula (IV) and
- c) a radical initiator according to claim 23 capable of generating a free radical of formula (V)



wherein n , R_1 , R_2 , R_3 , R_{10} , R_{11} and R_{12} are as defined in claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/EP 98/04102

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F2/00 C08F2/38 C08F4/00 C07C239/20 C08F293/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 735 052 A (XEROX CORP) 2 October 1996 cited in the application see page 2, line 3-8 see page 7, line 21-41 ---	1-17
Y	EP 0 135 280 A (COMMW SCIENT IND RES ORG) 27 March 1985 see page 6, line 27 - page 7, line 29 & US 4 581 429 A (SOLOMON ET AL.) 8 April 1986 cited in the application ---	1-17
Y	BE 619 146 A (AMERICAN CYANAMID COMPANY) 19 December 1962 see page 3; formulae I and II see claims 2,3,5,6 --- -/-	1-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the international search

28 August 1998

Date of mailing of the international search report

17. 12. 1998

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Authorized officer

Rodriguez, L

INTERNATIONAL SEARCH REPORT

International Application No

PC:/EP 98/04102

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	B. A. GINGRAS, W. A. WATERS: "Properties and Reactions of Free Alkyl Radicals in Solution. Part VII. Reactions with Quinone Imides, Nitric Oxide and Nitroso-compounds." J. CHEM. SOC., 1954, pages 1920-1924, XP002050740 cited in the application see page 1920; formulae III and IV see table 1	1-17
Y	--- CHEMICAL ABSTRACTS, vol. 54, no. 14, 25 July 1960 Columbus, Ohio, US; abstract no. 14163h, page 14163; XP002050752 see abstract & B. A. GINGRAS, C. H. BAYLEY: "Preparation of some fluorine-containing trisubstituted aromatic hydroxylamines." CAN. J. CHEM., vol. 37, 1959, pages 988-992, ---	1-17
Y	--- IWAMURA M ET AL: "REACTIONS OF NITRONES WITH FREE RADICALS. I. RADICAL 1,3-ADDITION TO NITRONES" BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, vol. 43, no. 3, March 1970, pages 856-860, XP002050758 cited in the application see compounds I to VIII; Table 2 -----	1-17

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 98/04102

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

See further information

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-17

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-17

A polymerisable composition comprising an ethylenically unsaturated monomer and a compound of formula (I), a process to carry out the polymerisation of this polymerisable composition and the polymer obtained by this process.

2. Claims: 18-21, 23-27

A compound of formula (I), a process for its preparation and its use in a process for polymerising ethylenically unsaturated monomers.

3. Claim : 22

A compound of formula (IV).

4. Claim : 28

A polymerisable composition comprising an ethylenically unsaturated monomer, a compound of formula (IV) and a source of free radicals of formula (V).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/04102

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0735052 A	02-10-1996	US 5608023 A JP 8269108 A	04-03-1997 15-10-1996
EP 0135280 A	27-03-1985	AU 571240 B DE 3486145 A JP 1797643 C JP 5006537 B JP 60089452 A US 4581429 A AU 3037884 A	14-04-1988 17-06-1993 28-10-1993 26-01-1993 20-05-1985 08-04-1986 17-01-1985
BE 619146 A		NONE	

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